

PATENT ABSTRACTS OF JAPAN

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(54) HEAT-SENSITIVE RECORDING MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a heat-sensitive recording material which has highly lustrous properties and prevents a head from being stained and can stably output an image with high quality.

SOLUTION: In the heat-sensitive recording material which successively has a heat-sensitive recording layer and a protective layer comprising a long chain alkyl ether-modified polyvinyl alcohol and at least two kinds of inorganic ultra-fine particles with different particle diameters on a substrate, the heat-sensitive recording material is characterized by two kinds of the inorganic ultra-fine particles being barium sulfate with a mean particle diameter of 0.05-0.20 μ m and a colloidal silica with a mean particle diameter of 10-50 nm and the colloidal silica being 8-24 mass% to the barium sulfate.

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CLAIMS

[Claim(s)]

[Claim 1] The thermal recording ingredient which it is the thermal recording ingredient which has a heat-sensitive recording layer and a protective layer containing long-chain alkyl ether denaturation polyvinyl alcohol and two or more sorts of inorganic ultrafine particles from which particle size differs one by one on a base material, and two sorts of said inorganic ultrafine particle are the barium sulfate of 0.05-0.20 micrometers of mean diameters, and colloidal silica of 10-50nm of mean diameters, and is characterized by doing 8-24 mass % content of said colloidal silica to a barium sulfate.

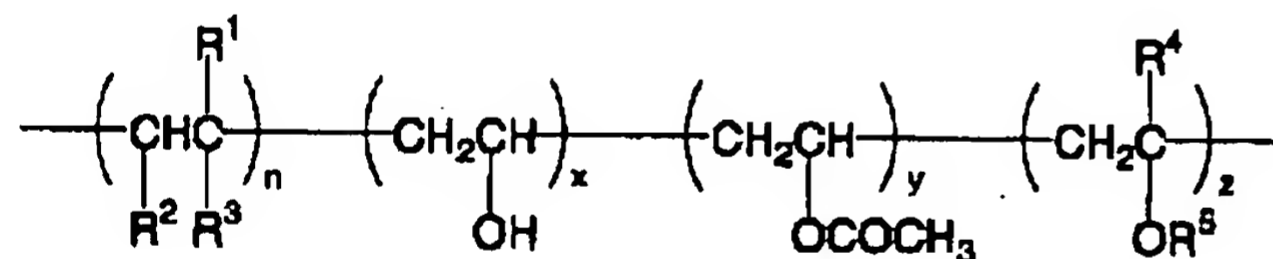
[Claim 2] The thermal recording ingredient according to claim 1 whose contact angle over the water of the print side after a print is 85 degrees or more.

[Claim 3] The thermal recording ingredient according to claim 1 or 2 whose long-chain alkyl ether denaturation polyvinyl alcohol is alkyl ether denaturation polyvinyl alcohol which has the alkyl group of carbon numbers 8-20.

[Claim 4] The thermal recording ingredient according to claim 1 to 3 which is the polymer which long-chain alkyl ether denaturation polyvinyl alcohol becomes from the following general formula (Z).

[Formula 1]

一般式 (Z)



R1 expresses a hydrogen atom, a methyl group, or -CH₂CO₂M among a general formula (Z), R2 expresses a hydrogen atom or -CO₂M, R3 expresses the radical which has a hydrogen atom, -CO₂M, the amino group, an amide group, a permutation amide group, a hydroxy group, a glycidyl group, a sulfonic group, a polyethylene oxide radical, polypropylene oxide radicals, or these functional groups, R4 expresses a hydrogen atom or a methyl group, and R5 expresses the alkyl group of the carbon atomic numbers 8-20. M expresses a hydrogen atom, an alkyl group, an aryl group, an aralkyl radical, and Na, K or Li. nx, y, and z express polymerization degree, respectively.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the thermal recording ingredient which records an image using a thermal head.

[0002]

[Description of the Prior Art] In facsimile, the printer, the label, etc., probably in a field, needs have expanded the thermal recording system, and the more highly efficient thermal recording ingredient is called for in connection with it. It is important with the thermal recording ingredient which heats in the image by this thermal head, and records an image, it not only has the head matching nature suitable for the quality of the material, a configuration, etc. of a protective coat of a thermal head, but that it can be stabilized and can output the image of high quality, without generating head dirt and head wear.

[0003] The protective layer which is mainly in the maximum upper layer determines the thermal head fitness of such a thermal recording ingredient, and various examination is carried out about the protective layer for some time. For example, in order to prevent with [to the head by sticking] a beam etc. and to give print fitness, in order to mitigate the dirt of a head further, it is required [addition of a pigment is indispensable, and] to increase the ratio of a pigment or to enlarge particle size of a pigment etc. However, the increment in the ratio of a pigment and expansion of particle size cause the fall of the glossiness by the fall of the smooth nature of the front face of a protective layer etc. as a result, and deterioration of quality produces them. Moreover, by the increment in oxygen permeability, when a diazo compound is used as a color coupler, increase of light exposure natural complexion coloring is also caused.

[0004] On the other hand, in order to carry out the print of the same side 3 times in succession [unlike the usual thermal recording ingredient / are a high speed and high energy and], the skin temperature of a head rises and it is very easy to generate head dirt with a full color thermal recording ingredient from the lubricant of a thermal recording ingredient front face decreasing in number by this at every print etc. However, on quality, since installation of the above general knowledge (increase the ratio of a pigment or enlarge particle size of a pigment) was difficult in order to realize high surface gloss and low light exposure natural complexion coloring, it was a very big technical problem to prevent head dirt etc. and to manufacture the thermal recording ingredient which can be stabilize and can output a high-definition image.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, this invention makes it a technical problem to attain this purpose for the purpose of preventing head dirt and offering the thermal recording ingredient which is stabilized and can output a high-definition image while it is made in view of the above-mentioned trouble and has high glossiness.

[0006]

[Means for Solving the Problem] <1> It is the thermal recording ingredient which has a heat-sensitive recording layer and a protective layer containing long-chain alkyl ether denaturation polyvinyl alcohol

and two or more sorts of inorganic ultrafine particles from which particle size differs one by one on a base material, and two sorts of said inorganic ultrafine particle are the barium sulfate of 0.05-0.20 micrometers of mean diameters, and colloidal silica of 10-50nm of mean diameters, and said colloidal silica is the thermal recording ingredient characterized by being carried out 8-24 mass % content to a barium sulfate.

[0007] <2> The contact angle over the water of the print side after a print is a thermal recording ingredient given in <1> which is 85 degrees or more.

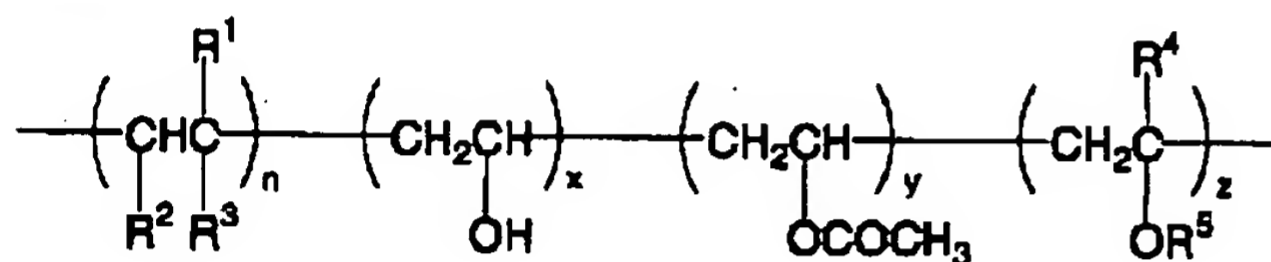
<3> <1> whose long-chain alkyl ether denaturation polyvinyl alcohol is alkyl ether denaturation polyvinyl alcohol which has the alkyl group of carbon numbers 8-20, or thermal recording ingredient given in <2>.

<4> Long-chain alkyl ether denaturation polyvinyl alcohol is the thermal recording ingredient according to claim 1 to 3 which is the polymer which consists of the following general formula (Z).

[0008]

[Formula 2]

一般式 (Z)



[0009] R1 expresses a hydrogen atom, a methyl group, or -CH₂CO₂M among a general formula (Z), R2 expresses a hydrogen atom or -CO₂M, R3 expresses the radical which has a hydrogen atom, -CO₂M, the amino group, an amide group, a permutation amide group, a hydroxy group, a glycidyl group, a sulfonic group, a polyethylene oxide radical, polypropylene oxide radicals, or these functional groups, R4 expresses a hydrogen atom or a methyl group, and R5 expresses the alkyl group of the carbon atomic numbers 8-20. M expresses a hydrogen atom, an alkyl group, an aryl group, an aralkyl radical, and Na, K or Li. nx, y, and z express polymerization degree, respectively.

[0010]

[Embodiment of the Invention] Two sorts of two or more sorts of inorganic ultrafine particles from which the thermal recording ingredient of this invention has a heat-sensitive recording layer, and long-chain alkyl ether denaturation polyvinyl alcohol and the protective layer containing two or more sorts of inorganic ultrafine particles from which particle size differs one by one on a base material, and said particle size differs are the barium sulfate of 0.05-0.20 micrometers of mean diameters, and colloidal silica of 10-50nm of mean diameters, and the colloidal silica of the content rate is eight to 24 mass % to a barium sulfate.

[0011] By using long-chain alkyl ether denaturation polyvinyl alcohol as a binder of a protective layer, the dispersibility of an inorganic ultrafine particle can be raised, the smooth nature of a thermal recording ingredient front face can be maintained, and the glossy fall by addition of an inorganic ultrafine particle can be controlled. Moreover, a high degree of hardness can be held by using colloidal silica with a minute particle size, without changing surface smooth nature. Furthermore, although there is a case where lubricant is spread and it becomes impossible to hold lubricant on a thermal recording ingredient front face, only by colloidal silica since the hydrophilic property is high, the lubricant of an initial complement can be made to stabilize and exist in a thermal recording ingredient front face by using a barium sulfate together. Thus, by holding a degree of hardness with the high front face, and stabilizing lubricant on the front face and existing in it, the thermal recording ingredient of this invention prevents the dirt of a head, can be stabilized and can output a high-definition image while it maintains the smooth nature of the front face and is high gloss.

[0012] In addition, in the thermal recording ingredient of this invention, you may have the layer of others which were suitably chosen according to the purpose, for example, the under coat prepared between said base materials and said heat-sensitive recording layers, the interlayer who prepares among

said heat-sensitive recording layers, the light transmittance adjustment layer prepared between said heat-sensitive recording layers and said protective layers between said base materials and said protective layers.

[0013] Hereafter, the thermal recording ingredient of this invention is explained in detail.

(Protective layer) It is the layer prepared in order that a protective layer may protect sticking of a heat-sensitive recording layer, and a heat-sensitive recording layer from a solvent etc., and this protective layer contains long-chain alkyl ether denaturation polyvinyl alcohol and two or more sorts of inorganic ultrafine particles from which particle size differs as mentioned above. Two sorts of this inorganic ultrafine particle are a barium sulfate and colloidal silica, 0.05-0.20 micrometers of mean particle diameter of a barium sulfate are 0.10-0.15 micrometers preferably, and 10-50nm of 10-30nm of mean particle diameter of colloidal silica is 15-25nm more preferably. moreover, colloidal silica -- a barium sulfate -- receiving -- eight to 24 mass % -- desirable -- eight to 16 mass % -- it is made still more desirable 8-10 mass % content.

[0014] When there is no particle size of a barium sulfate and colloidal silica in the above-mentioned range and there is no content rate of a barium sulfate and colloidal silica in the above-mentioned range, the case where high gloss is unmaintainable arises, and head dirt becomes remarkable, and it becomes difficult to form many images convenient. Moreover, as for the thermal recording ingredient of this invention, it is desirable that the contact angle over the water of the print side after a print is 85 degrees or more, and it is more desirable that it is 87 degrees or more. This contact angle can be stabilized in lubricant on a thermal recording ingredient (protective layer) front face as it is less than 85 degrees, and it cannot make it exist.

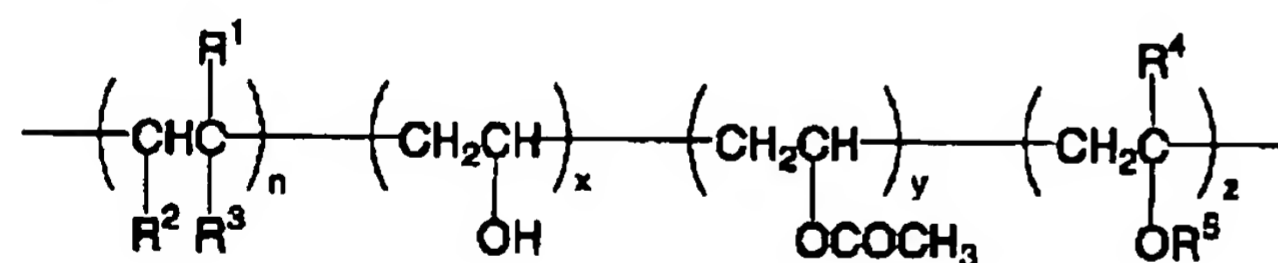
[0015] It is defined as this contact angle by JIS-K3211, and can measure as a measuring method with the contact angle meter made from Consonance Interface Science (FACE contact angle meter CA-D) etc., for example. In addition, it is desirable to also make a protective layer contain other pigments, waxes, a cross linking agent, a catalyst, a release agent, a surfactant, water repellent, etc. other than said inorganic ultrafine particle (pigment) if needed.

[0016] As for the long-chain alkyl ether denaturation polyvinyl alcohol used by this invention, it is desirable that it is alkyl ether denaturation polyvinyl alcohol which has the alkyl group of the carbon atomic numbers 8-20, and it is more desirable that it is the polymer which consists of the following general formula (Z) further.

[0017]

[Formula 3]

一般式 (Z)



[0018] R1 expresses a hydrogen atom, a methyl group, or -CH₂CO₂M among said general formula (Z), R2 expresses a hydrogen atom or -CO₂M, R3 expresses the radical which has a hydrogen atom, -CO₂M, the amino group, an amide group, a permutation amide group, a hydroxy group, a glycidyl group, a sulfonic group, a polyethylene oxide radical, polypropylene oxide radicals, or these functional groups, and R4 expresses a hydrogen atom or a methyl group. The combination R1, R2, and whose R4 are hydrogen atoms and whose R3 is -CO₂M, or the combination R2 and whose R4 are hydrogen atoms, whose R1 is -CH₂CO₂M and whose R3 is -CO₂M is desirable.

[0019] M expresses a hydrogen atom, an alkyl group, an aryl group, an aralkyl radical, and Na, K or Li. R5 expresses a long-chain alkyl group, i.e., the alkyl group of the carbon atomic numbers 8-20. A straight chain or branching is sufficient as an alkyl group, and it may have substituents, such as an aryl group. Also in this, the alkyl group of carbon numbers 8-16 is more desirable in respect of lubricity, and especially the dodecyl of the carbon atomic number 12 is desirable.

[0020] nx, y, and z express polymerization degree, respectively. As for n, 0-20 are desirable, and 0-10 are more desirable. When the value of n is large, an acidic group increases and compatibility with gelatin improves. As for x, 60-99 are desirable, and 75-95 are more desirable at the point which can pull out the properties of polyvinyl alcohol, such as gas barrier property below Tg (glass transition point). As for y, 0-20 are desirable. Although abrasion resistance with a thermal printing head and the larger one of z in respect of lubricity are desirable, it is limited in respect of the viscosity of solubility and a water solution, and 0.5 - 10% of its value is desirable to total of nx, y, and z, and it is 1 - 5% more preferably.

[0021] As Tg of these long-chain alkyl ether denaturation polyvinyl alcohol, 50 degrees C or more are 60 degrees C or more preferably. When Tg (glass transition point) is less than 50 degrees C, damage resistance falls and it is not desirable.

[0022] In the protective layer in the thermal recording ingredient of this invention, long-chain alkyl ether denaturation polyvinyl alcohol contains more than 80 mass % preferably more than 50 mass %. The property by the long-chain alkyl ether denaturation polyvinyl alcohol which the content of long-chain alkyl ether denaturation polyvinyl alcohol described above under by 50 mass % may not fully be demonstrated.

[0023] The orientation of the long-chain alkyl group is easy to be carried out to the front face of a protective layer using the long-chain alkyl ether denaturation polyvinyl alcohol of this invention. Such a front face reduces the dynamical friction of the head for a sensible heat, the print failure of it is lost, and improvement in the smooth nature (glossiness) of a print side and improvement in coloring concentration of it are attained. Moreover, the fall of surface statical friction and dynamical friction makes performance traverse of the media in a printer good. Furthermore, since the hydrophobic radical is carrying out orientation to the front face, its water resisting property also improves, while long-chain alkyl ether denaturation polyvinyl alcohol demonstrates the lightfastness which is the description of a polyvinyl alcohol system, and the property of excelling in coat reinforcement.

[0024] In a protective layer, other aquosity binder components other than long-chain alkyl ether denaturation polyvinyl alcohol may be used together if needed. As other aquosity binder components A silicone denaturation polymer, gelatin, methyl cellulose, a carboxymethyl cellulose, Hydroxyethyl cellulose, starch, an agar, kappa-carrageenan, Gum arabic, casein, styrene maleic anhydride copolymer hydrolyzate, Ethylene-maleic-anhydride copolymer hydrolyzate, isobutylene-maleic-anhydride copolymer hydrolyzate, polyvinyl alcohol, denaturation polyvinyl alcohol, polyacrylamide, etc. are mentioned.

[0025] Also in these aquosity binders, a silicone denaturation aquosity polymer and ethylene denaturation polyvinyl alcohol are desirable. The thing of a publication is mentioned [Japanese Patent Application No. / No. 7060 / nine to] as an example of said silicone denaturation aquosity polymer. Especially, especially the silicone block denaturation polyvinyl alcohol that used polyvinyl alcohol for the trunk polymer is desirable. Moreover, about ethylene denaturation polyvinyl alcohol, it mentions later.

[0026] Also in these, in the natural complexion section and a print side, surface smooth nature is high, it is the point of excelling in glossiness and the water-soluble polymer in which set desiccation is possible is suitable. In the time of heating (for example, before or after 40 degrees C), the water-soluble polymer in which set desiccation is possible presents predetermined viscosity, spreading of it is attained, if it cools after that (for example, 5 degrees C - 15 degrees C), viscosity rises and it means the water-soluble polymer which a flow condition stops and gels. As a polymer suitable as a water-soluble polymer in which set desiccation is possible, polysaccharide, such as protein, such as gelatin, carrageenan, and an agar, a polyvinyl alcohol system compound, etc. are mentioned, and when it is a polyvinyl alcohol system compound, it can be used as a water-soluble polymer in which set desiccation is possible by using together with the way acid as a polyvinyl alcohol system compound and a gelling agent, or its salt.

[0027] As other aquosity binders, synthetic rubber latex or a synthetic-resin emulsion can also be used. As a monomer which constitutes the latex and emulsion of these polymers, acrylic ester, methacrylic ester, crotonic-acid ester, vinyl ester, diester maleate, fumarate diester, itaconic-acid diester,

acrylamides, methacrylamide, vinyl ether, styrene, acrylonitrile, etc. are mentioned, for example.

[0028] If an example is further shown about these monomers, as acrylic ester, methyl acrylate, ethyl acrylate, n-propylacrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, acetoxymethyl acrylate, phenyl acrylate, 2-methoxy acrylate, 2-ethoxy acrylate, 2-(2-methoxyethoxy) ethyl acrylate, etc. will be mentioned.

[0029] As methacrylic ester, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, 2-hydroxyethyl methacrylate, 2-ethoxyethyl methacrylate, etc. are mentioned. As crotonic-acid ester, crotonic-acid butyl, crotonic-acid hexyl, etc. are mentioned. As vinyl ester, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl methoxy acetate, benzoic-acid vinyl, etc. are mentioned.

[0030] As diester maleate, a diethyl maleate, maleic-acid dimethyl, dibutyl maleate, etc. are mentioned. As fumarate diester, diethyl fumarate, dimethyl fumarate, fumaric-acid dibutyl, etc. are mentioned. As itaconic-acid diester, itaconic-acid diethyl, dimethyl itaconate, dibutyl itaconate, etc. are mentioned.

[0031] As acrylamides, acrylamide, methylacrylamide, ethyl acrylamide, propyl acrylamide, n-butyl acrylamide, tert-butyl acrylamide, cyclohexyl acrylamide, 2-methoxy ethyl acrylamide, dimethyl acrylamide, diethyl acrylamide, phenyl acrylamide, etc. are mentioned.

[0032] As methacrylamide, methyl methacrylamide, ethyl methacrylamide, n-butyl methacrylamide, tert-butyl methacrylamide, 2-methoxy methacrylamide, dimethyl methacrylamide, diethyl methacrylamide, etc. are mentioned.

[0033] As vinyl ether, the methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, methoxymethyl vinyl ether, dimethylamino vinyl ether, etc. are mentioned. As styrene, styrene, methyl styrene, dimethyl styrene, trimethyl styrene, ethyl styrene, isopropyl styrene, butyl styrene, chloromethyl styrene, methoxy styrene, butoxy styrene, acetoxymethyl styrene, chloro styrene, dichloro styrene, bromostyrene, vinyl benzoic-acid methyl ester, 2-methyl styrene, etc. are mentioned.

[0034] A homopolymer or a copolymer is sufficient as the polymer constituted by these monomers. The duality or the ternary polymerization object of acrylic ester, methacrylic ester, styrene, an acrylic acid, and a methacrylic acid; the copolymer of styrene and a butadiene is used preferably.

[0035] 150 degree C or less of 0 degree C - 130 degree C of Tg(s) of the macromolecule which constitutes an aqueous binder (glass transition point) are 40 degrees C - 100 degrees C especially preferably.

[0036] Moreover, it is desirable to use together the cross linking agent which carries out crosslinking reaction to a silicone denaturation polymer and/or an aqueous binder, and, as for a silicone denaturation polymer and/or an aqueous binder, it is desirable to have at least one sort of functional groups chosen from a carboxy group, the amino group, an ammonium salt radical, the hydroxy group, the sulfinic-acid (or the salt) radical, the sulfonic-acid (or the salt) radical, or the glycidyl group as a functional group.

[0037] As the above-mentioned cross linking agent, a vinyl sulfone system compound, aldehyde system compounds (formaldehyde, glutaraldehyde, etc.), epoxy compound, an oxazine system compound, triazine compound, a giant-molecule hardening agent given in JP,62-234157,A, a methylation melamine, blocked isocyanate, a methylol compound, carbodiimide resin, etc. can be used, for example.

[0038] Also in these cross linking agents, the macromolecule hardening agent of a publication is suitable for a vinyl sulfone system compound, an aldehyde system compound, epoxy compound, an oxazine system compound, triazine compound, and JP,62-234157,A.

[0039] Moreover, especially in denaturation polyvinyl alcohol, although this can raise a water resisting property etc. by itself, in order to raise a water resisting property further, use of the catalyst which promotes a cross linking agent and its reaction with silanol denaturation polyvinyl alcohol is effective [silanol denaturation polyvinyl alcohol is desirable, and].

[0040] The following are mentioned as a concrete cross linking agent. As an epoxy compound, the thing of two or more organic functions can be used. For example, dibromomethyl phenyl glycidyl ether, Dibromoneopentylglycol diglycidyl ether, the emulsion of epoxy cresol novolak resin, A denaturation bisphenol A mold epoxy emulsion, adipic-acid diglycidyl ester, o-FUTARU acid JIKURISHIJIRU ester, hydroquinone diglycidyl ether, Bisphenol S glycidyl ether, terephthalic-acid diglycidyl ether, A glycidyl

phthalimide, propylene polypropylene glycol diglycidyl ether, Polytetramethylene glycol diglycidyl ether, allyl glycidyl ether, 2-ethylhexyl glycidyl ether, phenyl glycidyl ether, Phenol 5 (EO) Glycidyl ether, p-tertiarybutyl phenyl glycidyl ether, Lauryl alcohol (EO)15 glycidyl ether, the glycidyl ether of the alcoholic mixture of carbon numbers 12-13, Glycerol polyglycidyl ether, trimethylolpropane polyglycidyl ether, Resorcinol diglycidyl ether, neopentyl glycol diglycidyl ether, 1, 6-hexanediol diglycidyl ether, ethylene polyethylene glycol diglycidyl ether, Sorbitol polyglycidyl ether, sorbitan polyglycidyl ether, Polyglycerol polyglycidyl ether, pentaerythritol polyglycidyl ether, Diglycerol polyglycidyl ether, triglycidyl-tris (2-hydroxyethyl) isocyanurate, etc. are mentioned, and glycidylethers are suitable also especially in these epoxy compounds.

[0041] The weight per epoxy equivalent of an epoxy compound effective in this invention has desirable 70-1000WPE. If weight per epoxy equivalent exceeds 1000WPE(s), it becomes difficult to give a water resisting property and it is not desirable.

[0042] Blocked isocyanate means the compound which masked the end isocyanate radical of isocyanate by the block agent. As blocked isocyanate, the block object of a hydrophilic radical which becomes the end of (a) isocyanate compound from a carbamoyl sulfonate radical (-NHCOSO₃-) is formed, for example. What blocked the activity isocyanate radical, the thing which blocked the activity isocyanate radical using (b) isopropylidene malonate (this blocked isocyanate is obtained at the reaction of HDI isocyanurate, isopropylidene malonate, and triethylamine.) What blocked the activity isocyanate radical by (c) phenols is mentioned.

[0043] By mixing [silanol denaturation polyvinyl alcohol and] such blocked isocyanate, and heating, bridge formation reforming of the silanol denaturation polyvinyl alcohol is carried out, and deck-watertight-luminaire-ization of silanol denaturation polyvinyl alcohol is attained. To a vinyl sulfone compound, what is carried by JP,53-57257,A, JP,53-41221,A, JP,49-13563,B, JP,47-24259,B, etc. is still more nearly usable.

[0044] As an aldehyde system compound, multiple-valued aldehydes, such as mono-aldehydes, such as formaldehyde and an acetaldehyde, glyoxal, glutaraldehyde, and dialdehyde starch (dialdehyde starch), etc. are mentioned, and a methylol melamine, a dimethylolurea, etc. are mentioned as a methylol compound. In the case of silanol denaturation polyvinyl alcohol, an aldehyde system compound is suitable for especially a cross linking agent.

[0045] It is desirable to carry out 1-50 mass section combination of the cross linking agent to the water-soluble polymer, polymer latex, or polymer emulsion 100 mass section as amount of the cross linking agent used to a water-soluble polymer, the above-mentioned polymer latex, or the above-mentioned polymer emulsion. Extent of bridge formation reforming is low in the loadings of a cross linking agent being under 1 mass section, and if a water resisting property, chemical resistance, etc. become inadequate and 50 mass sections are exceeded on the other hand, liquid ammonia quality falls and it is not desirable.

[0046] The inorganic ultrafine particle used by this invention has desirable zinc oxide, magnesium oxide, lead oxide, zirconium dioxide, and alumina other than colloidal silica and a barium sulfate, and especially its alumina is desirable.

[0047] As an inorganic ultrafine particle which can be used suitable for this invention, a barium sulfate (trade name: BARIFINE BF-21, BF-20, Sakai Chemical Industry make), colloidal silica (trade name: the Snow tex O, product made from Nissan Chemistry), a zirconium dioxide (trade name: NZR-A, product made from the Nissan chemistry), a zinc oxide (trade name: FINEX-75, Sakai Chemical Industry make), titanium oxide (TTO-55, Ishihara Sangyo make), and a silica (product made from Japanese Aerosil) are mentioned concretely.

[0048] As for said barium sulfate and colloidal silica, being contained more than 60 mass % is desirable among [all] an inorganic ultrafine particle, being contained more than 75 mass % is more desirable, and being contained more than 85 mass % is still more desirable. By containing this barium sulfate and colloidal silica more than 60 mass %, the effectiveness of this invention can be demonstrated effectively.

[0049] Here, although there will be especially no limit if the first [an average of] particle size says a

non-subtlety particle 0.15 micrometers or less more preferably and is such a non-subtlety particle 0.2 micrometers or less preferably 0.5 micrometers or less, 0.5 micrometers or less have the desirable maximum particle diameter (threshold with the larger particle size distribution in the inside of dispersion liquid) in dispersion liquid, an inorganic ultrafine particle has more desirable 0.4 micrometers or less, and especially its 0.35 micrometers or less are desirable. Moreover, the particle diameter in dispersion liquid is [the frequency of a particle (condensation) 0.35 micrometers or more] 1% or less preferably 5% or less, and it is desirable that the frequency of a particle (condensation) 0.25 micrometers or more is especially 5% or less. In addition, particle diameter is a well-known approach, for example, COULTER. It can measure with N4 mold submicron size analysis equipment (department machine of a day) etc. (The product made from Japanese Aerosil) is mentioned.

[0050] In order to prevent condensation of particles and to attain uniform adsorption on a resin particle front face as an approach of adding this inorganic ultrafine particle, it is desirable from a viewpoint on effectiveness and manufacture to adopt the approach of adding, after preparing the approach and colloidal dispersion object which are added as a resin solution with a carboxymethyl cellulose, gelatin, and water nature powder resin like polyvinyl alcohol with various mills etc. Moreover, it is a mass ratio, as for the blending ratio of coal (a binder / inorganic ultrafine particle) of a binder and an inorganic ultrafine particle, 0.8 / 0.5 - 0.8/0.15 are desirable, and 0.8 / 0.45 - 0.8/0.3 are more desirable.

[0051] In addition, to said protective layer, pigments, such as the stratified compound of the minerals containing a mica etc., a calcium oxide, a zinc oxide, titanium oxide, an aluminum hydroxide, a kaolin, synthetic silicate, amorphous silica, and urea formalin resin powder, may be added.

[0052] On the heat-sensitive recording layer which mentions later the coating liquid for protective layers which consists of a binder, an inorganic ultrafine particle, etc., a protective layer uses, applies and dries and obtains equipments, such as a bar coating machine, an air knife coating machine, a blade coating machine, and a curtain coating machine. However, a protective layer may be applied to a heat-sensitive recording layer etc. and coincidence by the superimposing method, and after spreading of a heat-sensitive recording layer etc., may once dry a heat-sensitive recording layer etc., and may be applied on it. The desiccation coverage of a protective layer has desirable 0.1 - 3 g/m², and its 0.3 - 2.0 g/m² is more desirable. If the amount of painting is large, heat sensitivity will fall remarkably, and in the too much low amount of painting, the functions (abrasion resistance, lubricity, damage resistance, etc.) as a protective layer cannot be demonstrated. Moreover, calender processing may be performed after protective layer spreading if needed.

[0053] (Heat-sensitive recording layer) Said heat-sensitive recording layer may be monolayer structure, may be multilayer structure, and can be made into the lamination suitably chosen according to the purpose. Including a coloring component, said heat-sensitive recording layer is designed so that a desired color image can be formed by the coloring reaction of this coloring component. As said coloring component, there is especially no limit and a well-known thing can use it suitably from the former. As said coloring reaction, there is especially no limit, for example, the coloring reaction of a diazonium salt compound and a coupler, the coloring reaction of an electron-donative colorlessness color and an electronic receptiveness compound, etc. are mentioned suitably.

[0054] When it contains the coupler which said heat-sensitive recording layer reacts at the time of said diazonium salt compound, this diazonium salt compound, and heat, and carries out coloration, the alkali which promotes the coloring reaction of this diazonium salt compound and this coupler is suitably added by this heat-sensitive recording layer.

[0055] Said diazonium salt compound is a compound expressed with the following general formula (B), and these can control the maximum absorption wavelength by the location and class of a substituent of Ar part.

General formula (B): Ar-N₂⁺X⁻ - In said general formula (B), Ar expresses an aryl group. X⁻ expresses an acid anion.

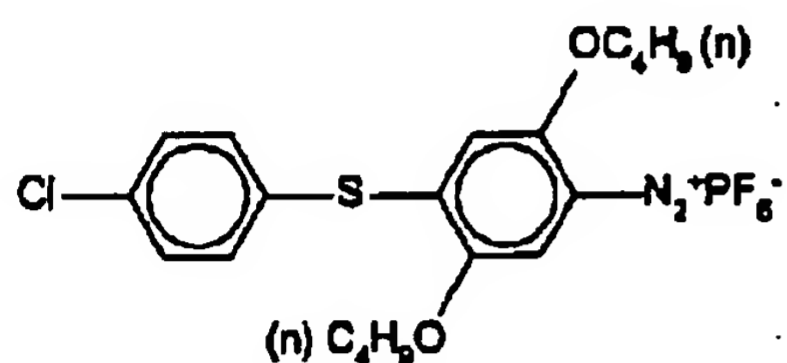
[0056] As an example of said diazonium salt compound 4-(N-(2-(2, 4-G tert-amyl phenoxy) butyryl) piperazino) benzene diazonium, 4-diocetyl aminobenzene diazonium, 4-(N-(2-ethyl hexa noil) piperazino) benzene diazonium, 4-dihexyl amino-2-hexyloxy benzene diazonium, 4-N - Ethyl-N-

hexadecyl amino-2-ethoxy benzodiazonium, 3 - Chloro-4-dioctylamino-2-octyl OKISHIO benzene diazonium, 2, 5-dibutoxy-4-morpholino benzene diazonium, 2, 5-octoxy-4-morpholino benzene diazonium, 2, 5-dibutoxy-4-(N-(2-ethyl hexa noil) piperazino) benzene diazonium, 2, 5-diethoxy-4-(N-(2-(2, 4-G tert-amyl phenoxy) butyryl) piperazino) benzene diazonium, An acid anion salt and the following diazonium salt compounds (D-1-5), such as 2, 5-dibutoxy-4-tolyl thio benzene diazonium, and 3-(2-octyloxy ethoxy)-4-MOROHORINO benzene diazonium, are mentioned. These may be used by the one-sort independent and may use two or more sorts together. Also in these, especially hexafluoro phosphate salt, tetrafluoroborate, 1, and 5-naphthalene sulfonate salt is desirable.

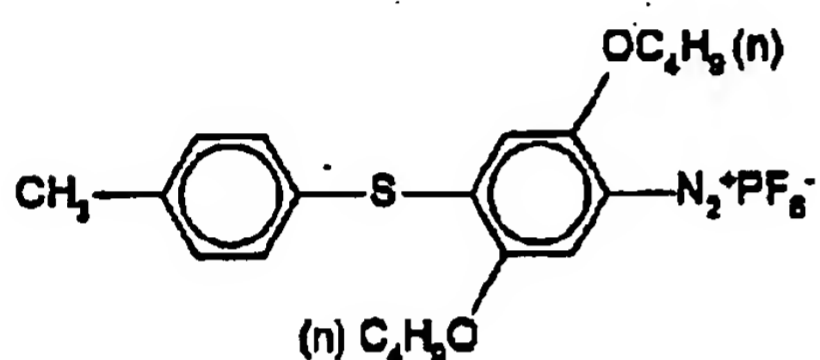
[0057]

[Formula 4]

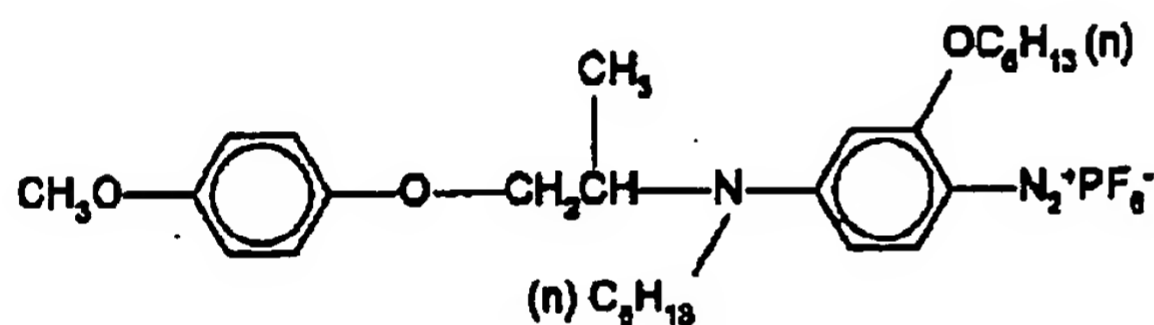
D-1



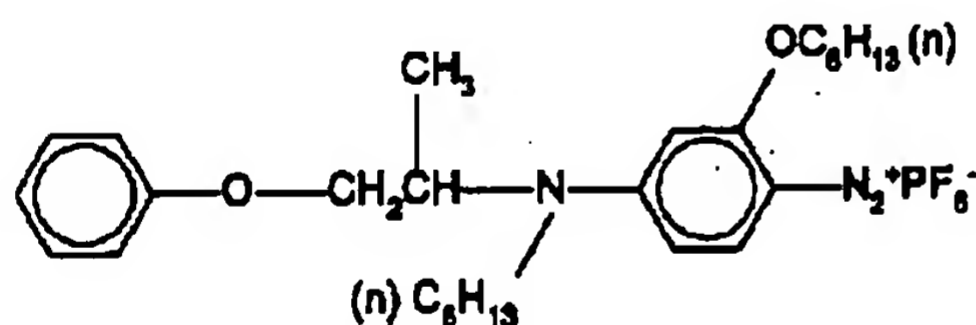
D-2



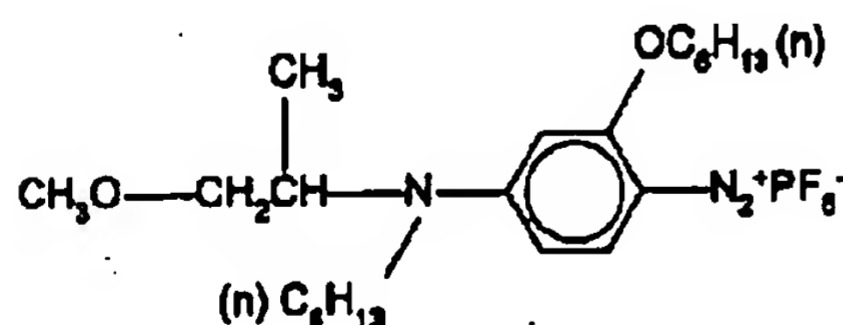
D-3



D-4



D-5



[0058] Also in these diazonium salt compounds, photodissociate by light with a wavelength of 300-400nm. 4-(N-(2-(2, 4-G tert-amyl phenoxy) butyryl) piperazino) benzene diazonium, 4-dioctyl aminobenzene diazonium, 4-(N-(2-ethyl hexa noil) piperazino) benzene diazonium, 4-dihexyl amino-2-hexyloxy benzene diazonium, 4-N - Ethyl-N-hexadecyl amino-2-ethoxy benzodiazonium, 2, 5-dibutoxy-4-(N-(2-ethyl hexa noil) piperazino) benzene diazonium, 2, 5-diethoxy-4-(N-(2-(2, 4-G tert-amyl phenoxy) butyryl) piperazino) benzene diazonium, and especially the diazonium salt compound shown in the above-mentioned example D-3-5 are desirable. In addition, the maximum absorption wavelength

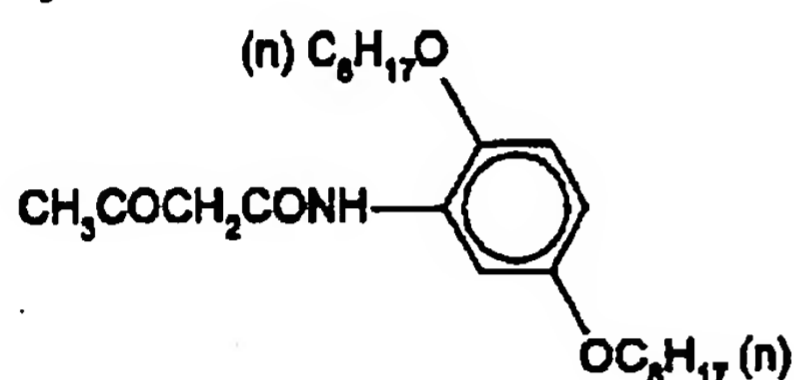
of a diazonium salt compound here measures with a spectrophotometer (Shimazu MPS-2000) what used each diazonium compound as the paint film by the coverage of 0.1 - 1.0 g/m².

[0059] As a coupler which reacts at the time of said diazonium salt compound and heat, and carries out coloration For example, resorcinol, full RUGURUSHIN, 2, 3-dihydroxy naphthalene-6-sulfonic-acid sodium, A 1-hydroxy-2-naphthoic-acid morpholino propyl amide, 1, 5-dihydroxy naphthalene, 2, 3-dihydroxy naphthalene, 2, 3-dihydroxy-6-sulfanil naphthalene, A 2-hydroxy-3-naphthoic-acid anilide, a 2-hydroxy-3-naphthoic-acid ethanol amide, A 2-hydroxy-3-naphthoic-acid octyl amide, 2 - Hydroxy-3-naphthoic-acid-N-dodecyloxy pull pill amide, A 2-hydroxy-3-naphthoic-acid tetradecyl amide, an acetanilide, Acetoacetanilide, a benzoyl acetanilide, 2-chloro-5-octyl acetoacetanilide, 1-phenyl-3-methyl-5-pyrazolone, a 1-(2'-octyl phenyl)-3-methyl-5-pyrazolone, A 1-(2', 4', 6'-TORIKURORO phenyl)-3-benzamide-5-pyrazolone, 1-(2', 4', 6'-TORIKURORO phenyl)-3-ANIRINO-5-PIRARON, a 1-phenyl-3-phenyl acetamide-5-pyrazolone, the compound shown in the following (C-1-6) are mentioned. These couplers may be used by the one-sort independent, and may be used together two or more sorts.

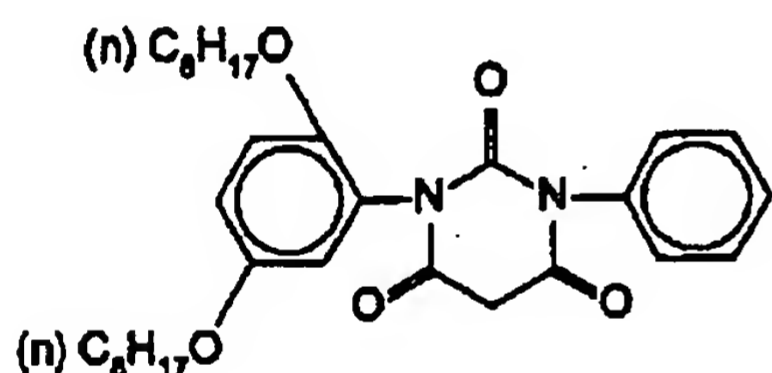
[0060]

[Formula 5]

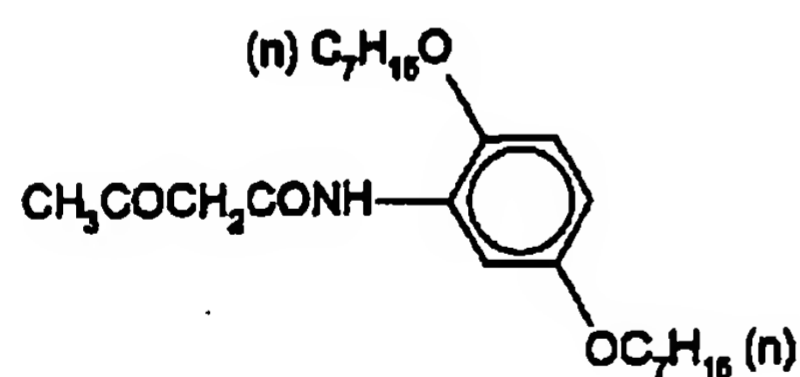
C-1



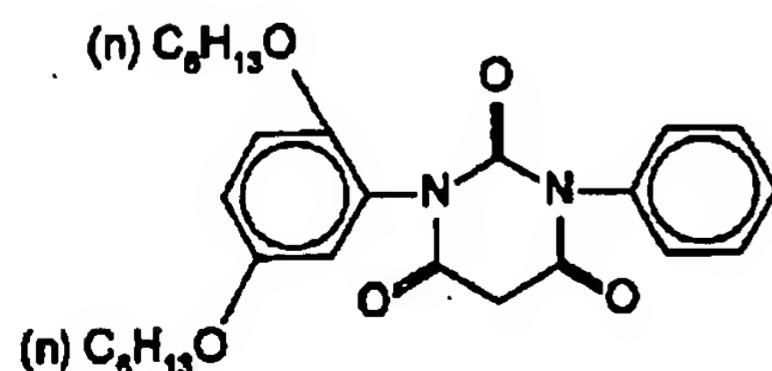
C-2



C-3



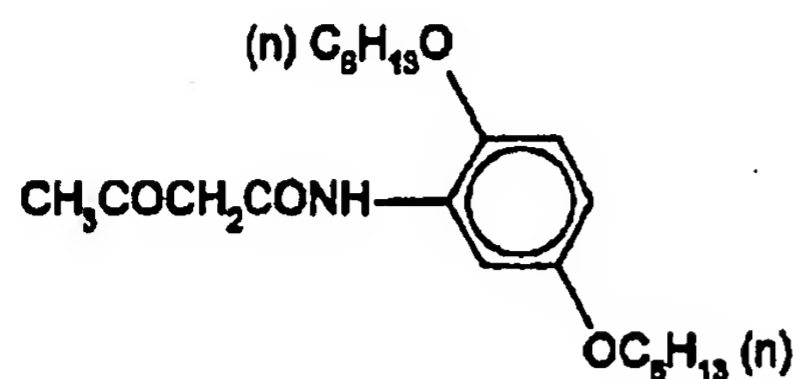
C-4



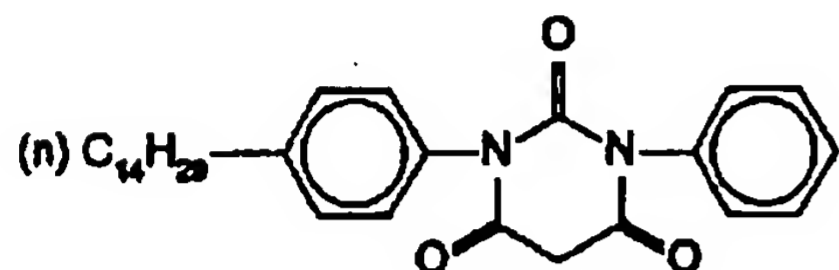
[0061]

[Formula 6]

C-5



C-6



[0062] As said alkali, there is especially no limit and it can be suitably chosen from well-known things according to the purpose. A compound which produces decomposition etc. and emits the alkali matter outside an inorganic or organic basic compound at the time of heating is also contained. As a typical thing To organic ammonium salt, an organic amine, an amide, a urea, and a thiourea pan, those derivatives, Nitrogen-containing compounds, such as thiazoles, pyrroles, pyrimidines, piperazines, guanidine, Indore, imidazole derivatives, imidazoline, triazoles, morpholines, piperidines, amidines, form azines, and pyridines, are mentioned.

[0063] As these examples, tricyclo hexylamine, tribenzylamine, Octadecyl benzylamine, a stearyl amine, allylurea, thiourea, A methylthio urea, allylthiourea, ethylenetiourea, 2-benzyl imidazole, 4-phenyl imidazole, 2-phenyl-4-methylimidazole, 2-undecyl imidazoline, 2 and 4, 5-TORIFURIRU-2-imidazoline, 1, 2-diphenyl -4, 4-dimethyl-2-imidazoline, 2-phenyl-2-imidazoline, 1, 2, 3-triphenyl guanidine, 1, 2-dicyclohexyl guanidine, 1, 2, 3-tricyclohexyl guanidine, a guanidine trichloroacetic-acid salt, A - dibenzyl piperazine, and N and N'4, 4'-dithio morpholine, a mol HORINIUMU trichloroacetic-acid salt, 2-amino benzothiazole, 2-benzoyl hydrazino benzothiazole, etc. are mentioned. These may be used by the one-sort independent and may use two or more sorts together.

[0064] As said electron-donative colorlessness color, there is especially no limit, and it can be suitably chosen from well-known objects according to the purpose, and an electron-donative colorlessness color precursor can be used in this invention.

[0065] As said electron-donative colorlessness color precursor, a thoria reel methane system compound, a diphenylmethane system compound, a thiazin system compound, a xanthene system compound, a SUPIRO pyran system compound, etc. are mentioned, for example. You may use it by the one-sort independent, and two or more sorts may be used together, also in these, these are the points that coloring concentration is high and useful, and a thoria reel methane system compound and a xanthene system compound are desirable. As these examples, 3 and 3-screw (p-dimethylamino phenyl)-6-dimethylamino phthalide (namely, crystal violet lactone), 3 and 3-screw (p-dimethylamino) phthalide, 3-(p-dimethylamino phenyl)-3-(1, 3-dimethyl Indore-3-IRU) phthalide, 3-(p-dimethylamino phenyl)-3-(2-methylindole-3-IRU) phthalide, 3-(o-methyl-p-diethylaminophenyl)-3-(2-methylindole-3-IRU) phthalide, 4 and 4'-screw (dimethylamino) BENZUHI drine compounds benzyl ether, N-halophenyl leuco auramine and N- 2, 4, and 5-TORIKUORO phenyl leuco auramine -- Rhodamine B-anilinolactam, a rhodamine (p-nitro ANIRINO) lactam, A rhodamine B-(p-chloroanilino) lactam, 2-benzylamino-6-diethylamino fluoran, 2-ANIRINO-6-diethylamino fluoran, 2-ANIRINO-3-methyl-6-diethylamino fluoran, 2-ANIRINO-3-methyl-6-cyclohexyl methylamino fluoran, 2-ANIRINO-3-methyl-6-isoamyl ethylamino fluoran, 2-(o-chloroanilino)-6-diethylamino fluoran, 2-octyl amino-6-diethylamino fluoran, 2-ethoxy ethylamino-3-chloro-2-diethylamino fluoran, 2-ANIRINO-3-chloro-6-diethylamino fluoran, benzoyl leuco methylene blue, p-nitrobenzyl leuco methylene blue, 3-methyl-spirodinaphthopyran, 3-ethyl-spirodinaphthopyran, 3,3'-dichlorospirodinaphthopyran, 3-benzylspirodinaphthopyran, a 3-propyl-spiro-dibenzo pyran, etc. are mentioned.

[0066] As said electronic receptiveness compound, a phenol derivative, salicylic acid derivatives, hydroxybenzoic-acid ester, etc. are mentioned. Also in these, bisphenols and especially hydroxybenzoic-acid ester are desirable. Specifically 2 and 2-screw (p-hydroxyphenyl) propane (namely, bisphenol A), 4 and 4'-(p-phenylene diisopropylidene) diphenol (Bisphenol [namely,] P), 2, and 2-screw (p-hydroxyphenyl) pentane, 2 and 2-screw (p-hydroxyphenyl) ethane, 2, and 2-screw (p-hydroxyphenyl) butane, 2 and 2-screw (4'-hydroxy-3', 5'-dichlorophenyl) propane, 1 and 1-(p-hydroxyphenyl) cyclohexane, 1, and 1-(p-hydroxyphenyl) propane, 1 and 1-(p-hydroxyphenyl) pentane, 1, a 1-(p-hydroxyphenyl)-2-ethyl hexane, 3 and 5-II (alpha-methylbenzyl) salicylic acid and its polyvalent metallic salt, 3 and 5-II (tert-butyl) salicylic-acid and its polyvalent-metallic-salt, 3-alpha, and alpha-dimethylbenzyl salicylic acid and its polyvalent metallic salt, Para-hydroxybenzoic-acid butyl, para-hydroxybenzoic-acid benzyl, para-hydroxybenzoic-acid-2-ethylhexyl, p-phenylphenol, especially p-cumyl phenol, etc. are desirable.

[0067] As for said heat-sensitive recording layer, in this invention, it is desirable to contain a sensitizer. As this sensitizer The low-melt point point organic compound which has the radical and polar group of aromaticity moderately in intramolecular is desirable. Specifically p-benzyloxy benzyl benzoate, alpha-naphthyl benzyl ether, beta-naphthyl benzyl ether, beta-naphthoic-acid phenyl ester, alpha-hydroxy-beta-naphthoic-acid phenyl ester, the beta-naphthol-(p-chloro benzyl) ether, 1,4-butanediol phenyl ether, 1,4-butanediol-p-methylphenyl ether, 1,4-butanediol-p-ethyl phenyl ether, 1,4-butanediol-m-methylphenyl ether, 1-phenoxy-2-(p-tolyloxy) ethane, 1-phenoxy-2-(p-ethyl phenoxy) ethane, 1-phenoxy-2-(p-chloro phenoxy) ethane, p-benzyl biphenyl, etc. are mentioned.

[0068] Moreover, as for a heat-sensitive recording layer, it is desirable to contain the compound expressed with the following general formula (A) two or more 0.05 g/m. Although there is especially no limit as a layer which the compound expressed with a general formula (A) contains and it can choose suitably according to the purpose when a heat-sensitive recording layer consists of two or more layers, it is desirable that it is the layer which consists of solid-state distribution objects.

[0069] General formula (A): In the R-SO₃M aforementioned general formula (A), R expresses an alkyl group, an aryl group, an alkoxyl group, an aryloxy group, a polyoxyethylene aryl group, or a polyoxyethylene alkyl group, its alkyl group of carbon numbers 1-20 is desirable, its aryl group of carbon numbers 1-30 is desirable, its alkoxyl group of carbon numbers 1-20 is desirable, its aryloxy group of carbon numbers 1-30 is desirable, its polyoxyethylene aryl group of carbon numbers 1-30 is desirable, and its polyoxyethylene alkyl group of carbon numbers 1-20 is desirable. M expresses alkali metal and sodium, its potassium, etc. are desirable.

[0070] As an example of a compound expressed with said general formula (A) Sodium lauryl sulfate, a higher-alcohol sodium sulfate, sodium dodecylbenzenesulfonate, Alkyl naphthalene sulfonic-acid sodium, the dialkyl sulfo sodium succinate, Alkyl diphenyl ether disulfon acid sodium, polyoxyethylene lauryl ethereal sulfate sodium, A polyoxyethylene-alkyl-ether sodium sulfate, a polyoxyethylene-alkyl-phenyl-ether sodium sulfate, The sodium salt of alkane sulfonic-acid sodium and beta-naphthalene sulfonic-acid formalin condensate, the sodium salt of a special aromatic series sulfonic-acid formalin condensate, etc. are mentioned. These may be used by the one-sort independent and may use two or more sorts together. In this invention, it is the point that light exposure coloring of the natural complexion section is improvable also in these, and sodium dodecylbenzenesulfonate expressed with the following formula is desirable.

[0071]

[Formula 7]



[0072] As a content in said heat-sensitive recording layer of the compound expressed with said general formula (A), it is two or more 0.05 g/m, and 0.05 - 0.50 g/m² is desirable, and 0.05 - 0.20 g/m² is desirable. The lightfastness of a thermal recording ingredient is not enough in it being less than two 0.05 g/m, and said content is desirable at the point that it is not such in on the other hand it being 0.05 g/m²

preferably at the point which natural complexion light exposure coloring produces, the weatherability of a thermal recording ingredient is improved remarkably, and natural complexion light exposure coloring is controlled effectively.

[0073] Said coupler which reacts at the time of said diazonium salt compound in said heat-sensitive recording layer, this diazonium salt compound, and heat, and carries out coloration, Said alkali, said electron-donative colorlessness color, said electronic receptiveness compound, There is especially no limit about the mode of content, such as said sensitizer, and it can choose suitably according to the purpose. for example, -- these -- (-- one --) -- a solid-state -- distribution -- depending -- containing -- making -- an approach -- (-- two --) -- emulsification -- distribution -- containing -- making -- an approach -- (-- three --) -- a polymer -- distribution -- containing -- making -- an approach -- (-- four --) -- a latex -- distribution -- containing -- making -- an approach -- (-- five --) -- microencapsulation -- carrying out -- containing -- making -- an approach -- etc. -- mentioning -- having .

[0074] The approach of making it microencapsulate and contain from a viewpoint of shelf life also in these is desirable, and it is desirable to microencapsulate said diazonium salt compound and to make it contain all over said heat-sensitive recording layer, when using the coloring reaction of said diazonium salt compound and said coupler, and when using the coloring reaction of said electron-donative colorlessness color and said electronic receptiveness compound, it is desirable to microencapsulate said electron-donative colorlessness color and to make it contain all over said heat-sensitive recording layer.

[0075] When making said heat-sensitive recording layer into multilayer structure, a multicolor thermal recording ingredient can be obtained by changing the hue of each heat-sensitive recording layer. Although there is especially no limit and it can be suitably chosen as lamination in this case according to the purpose Two sorts of diazonium salt compounds with which sensitization wavelength differs in this invention, It is desirable to consider as the multicolor heat-sensitive recording layer which carried out the laminating of the heat-sensitive recording layer which combined the heat-sensitive recording layer two-layer which combined the coupler which reacts at the time of each diazonium salt compound and heat, and colors to a different hue, and an electron-donative colorlessness color and an electronic receptiveness compound. Namely, the heat-sensitive recording layer A which contains an electron-donative colorlessness color and an electronic receptiveness compound on said base material It reacts at the time of the diazonium salt compound and this diazonium salt compound whose maximum absorption wavelength is $360 \pm 20\text{nm}$, and heat. The multicolor thermal recording ingredient which carried out the laminating of the heat-sensitive recording layer B-1 containing the coupler which carries out coloration, and the heat-sensitive recording layer B-2 containing the coupler which reacts at the time of the diazonium salt compound and this diazonium salt compound whose maximum absorption wavelength is $400 \pm 20\text{nm}$, and heat, and carries out coloration to this order is desirable.

[0076] A heat-sensitive recording layer B-2 is heated first, and the diazonium salt compound and coupler which are contained in this heat-sensitive recording layer B-2 are made to color as the record approach of this multicolor thermal recording ingredient. Next, after making the unreacted diazonium salt compound which irradiates $400 \pm 20\text{nm}$ light and is contained all over the heat-sensitive recording layer B-2 disassemble, a heat-sensitive recording layer B-1 applies sufficient heat to color, and makes the diazonium salt compound and coupler which are contained in this heat-sensitive recording layer B-1 color. At this time, although a heat-sensitive recording layer B-2 is also strongly heated to coincidence, since the diazonium salt compound is disassembled and coloring capacity is lost, coloring is not already carried out. The diazonium salt compound which irradiates further $360 \pm 20\text{nm}$ light, and is contained in the heat-sensitive recording layer B-1 is disassembled, and sufficient heat which a heat-sensitive recording layer A finally colors is made to apply and color. Although a heat-sensitive recording layer B-2 and a heat-sensitive recording layer B-1 are also strongly heated to coincidence at this time, since it has decomposed and coloring capacity is lost, a diazonium salt compound does not already color.

[0077] Moreover, in this invention, it is also desirable to consider as the multicolor heat-sensitive recording layer which carried out the laminating of the three layers of the heat-sensitive recording layers which combined the coupler which colors to a hue which reacted at the time of three sorts of diazonium salt compounds with which sensitization wavelength differs, each diazonium salt compound, and heat,

and is different. The maximum absorption wavelength 350nm or less on said base material namely, preferably It reacts at the time of the diazonium salt compound and this diazonium salt compound which are 340nm or less, and heat. It reacts at the time of the diazonium salt compound the heat-sensitive recording layer A-1 containing the coupler which carries out coloration, and whose maximum absorption wavelength are 360**20nm, this diazonium salt compound, and heat. The multicolor thermal recording ingredient which carried out the laminating of the heat-sensitive recording layer A-2 containing the coupler which carries out coloration, and the heat-sensitive recording layer A-3 containing the coupler which reacts at the time of the diazonium salt compound and this diazonium salt compound whose maximum absorption wavelength is 400**20nm, and heat, and carries out coloration to this order is desirable. In the case of the above multicolor heat-sensitive recording layer, if it chooses so that it may become the three primary colors [in / for the coloring hue of each heat-sensitive recording layer / subtractive color mixture], yellow, a Magenta, and cyanogen, full color image recording will become possible.

[0078] As said base material, for example Polyester film, such as polyethylene terephthalate and polybutylene terephthalate, (Base material) Cellulosic films, such as a triacetic-acid cellulose film, a polystyrene film, Polyolefine films, such as a polypropylene film and a polyethylene film, A polyimide film, a polyvinyl chloride film, a polyvinylidene chloride film, The base material which paper, a synthetic paper, the paper that has a plastic resin layer are mentioned outside plastic film, such as a polyacrylic acid copolymer film and a polycarbonate film, and has the layer of said plastic film is desirable. These may be transparent, and may be opaque, and may be used by the one-sort independent, and may use two or more sorts together.

[0079] As a base material which has the layer of said plastics Or that by which the layer by thermoplastics was formed in the field in which a recording layer is formed at least is mentioned suitably. both sides of stencil paper -- For example, that by which melting extrusion coating of the thermoplastics was carried out to (1) stencil paper, the thing which applied the gas barrier layer on the thermoplastics by which melting extrusion coating was carried out in (2) Hara paper, (3) That on which the low plastic film of oxygen permeability of stencil paper was pasted up, (4) After carrying out melting extrusion coating of the thermoplastics to what prepared thermoplastics by melting extrusion on the field which pasted up plastic film on stencil paper, and (5) stencil paper, that on which plastic film was pasted up is mentioned.

[0080] As thermoplastics by which melting extrusion coating is carried out to said stencil paper, olefin system polymers, such as mixture of the homopolymers of alpha olefins, such as polyethylene and polypropylene, and these polymers of various kinds of, the random copolymer of ethylene and vinyl alcohol, etc. are mentioned suitably, for example. As said polyethylene, LDPE (low density polyethylene), HDPE (high density polyethylene), L-LDPE (straight chain-like low density polyethylene), etc. are mentioned, for example.

[0081] As an approach of paste up said plastic film on said stencil paper, there be especially no limit, and it can choose suitably from well-known lamination processes which be indicate by the volume on processing technical study group "a new lamination handbook", and can adopt, and the dry lamination using the so-called dry lamination, a non-solvent mold dry lamination, an electron ray, or ultraviolet curing mold resin or a hot dry lamination be mention suitably. In this invention, especially the thing that coated with the olefin system polymer both sides of the stencil paper which uses natural pulp as a principal component also in said base material is desirable.

[0082] (Under coat) In this invention, it is desirable to have an under coat between said base materials and said heat-sensitive recording layers. although there is especially no limit and it can choose suitably from well-known things as said under coat according to the purpose -- PAGI -- the viscosity of law -- 10-30mP and PAGI -- it is desirable especially to contain the gelatin (for "gelatin" to only be called below) whose jelly strength of law is 15-70g, and a layer-like inorganic compound. In addition, in this invention, it is also desirable to have such a layer as the after-mentioned interlayer etc.

[0083] said PAGI -- the viscosity of law, and said PAGI -- the jelly strength of law -- PAGII of examination meeting [/ photographic gelatin examining method] issue -- law -- it measures based on

the :photographic gelatin examining method and the trial by the 7th edition (1992 editions). Said gelatin is obtained by carrying out depolymerize of the well-known gelatin ("usual gelatin" being called below) manufactured by the usual approach. However, the "usual gelatin" said here is for example, "glue and gelatin (raw materials, such as my Yoshihiro Sun-tzu edit, Japanese glue, a cow bone that is indicated by gelatin ***** (1987), oxbone, and a pig skin, are processed from lime, an acid, etc., and it is manufactured, and has far big viscosity and jelly strength compared with said gelatin.).

[0084] Said usual gelatin is characterized according to conditions, such as a raw material, an art (for example, liming, acid treatment), and an extraction condition (temperature, count of an extract).

Although said gelatin is carried out based on what kind of gelatin, and depolymerize of it may be carried out and it may be obtained, there are few counts of an extract and what was extracted at low temperature is desirable at a point compatible in said numeric-value within the limits in hypoviscosity and jelly strength. The method of the approach using an enzyme as the approach of said depolymerize, the approach using heat, etc. being mentioned, and using an enzyme also in these is desirable. In the case of the approach using said heat, when viscosity is lowered to a desirable value, said jelly strength may become low. In addition, as said enzyme, a papain is mentioned suitably, for example.

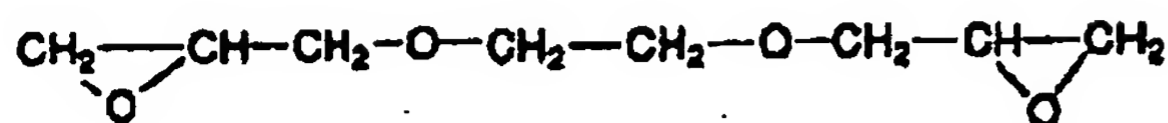
[0085] said PAGI in said gelatin -- the viscosity of law -- 10-30mP -- it is -- said PAGI -- although the jelly strength of law is 15-70g -- said PAGI -- if the viscosity down of coating liquid may become large, the distributed condition of the pigment in coating liquid (mica) may worsen, when the viscosity of law is less than 10 mPs, and 30mP is exceeded, the viscosity of coating liquid will rise and it will become easy to produce spreading failure moreover, said PAGI -- if the jelly strength of law is less than 15g, paint film reinforcement will fall and bond strength with said base material will fall -- it is -- said PAGI - - when the jelly strength of law is larger than 70g, curl of a paint film may become large by the environmental variation

[0086] Said gelatin may construct a bridge using a hardening agent if needed, and the well-known thing used as a hardening agent of gelatin as this hardening agent is mentioned in that case, for example, a vinyl sulfone compound, an activity halogenated compound, an isocyanate compound, an epoxy compound, etc. are mentioned. Also in these, especially an epoxy compound is desirable and the compound shown below is suitably mentioned as this epoxy compound, for example.

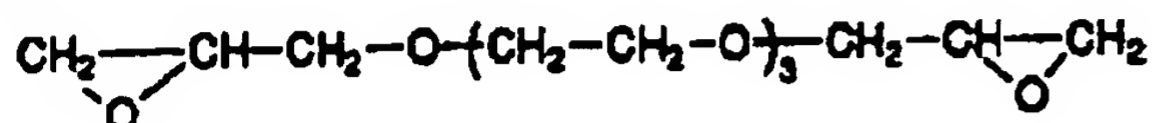
[0087]

[Formula 8]

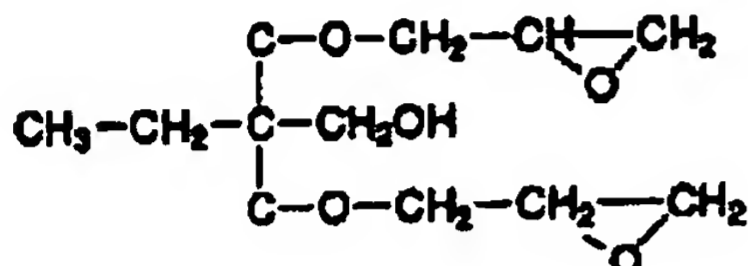
E-1



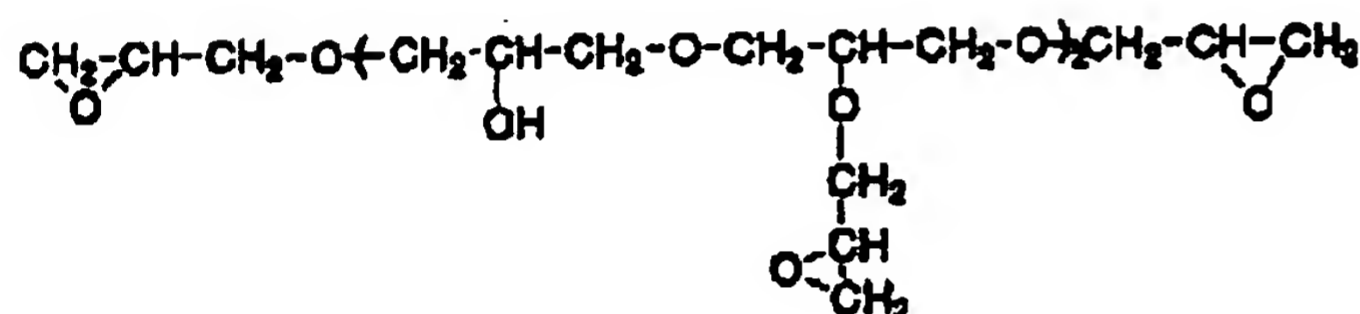
E-2



E-3



E-4



[0088] As coverage in said under coat of said gelatin, two or more 0.5 g/m is desirable from a viewpoint which stops PURISUTA (fine bulging phenomenon by the heat of the printer thermal head at the time of print record).

[0089] As an inorganic compound of the shape of said layer, a bloating tendency inorganic stratified compound is mentioned suitably. As an example of said bloating tendency inorganic stratified compound, bloating tendency viscosity minerals, such as a bentonite, hectorite, saponite, a BIDE light, nontronite, a SUCHIBUN site, beidellite, and a MOMMORI night, bloating tendency synthetic mica, a bloating tendency composition smectite, etc. are mentioned.

[0090] These bloating tendency inorganic stratified compounds have the laminated structure which thickness becomes from the unit crystal-lattice layer which is about 10-15Å, and its grid money-paid-on-account group atom permutation is remarkably larger than other clay minerals. Consequently, the latticed layer produces the lack of a forward electric charge, and in order to compensate it, it is adsorbing cations, such as Na⁺, calcium²⁺, and Mg²⁺, between layers. The cation which intervenes among these layers is called a "convertibility cation", and is exchanged for various cations. In Li⁺, Na⁺, etc., since the ionic radius is small, especially the cation between layers has weak association between lamellar crystal grids, and swells greatly by water. If SHIEA is applied in the condition, cleavage will be carried out easily, and the sol stabilized underwater is formed. Also in the example of said bloating tendency inorganic stratified compound, a bentonite and bloating tendency synthetic mica are desirable at the point that the inclination is strong, and especially its bloating tendency synthetic mica is desirable.

[0091] As said bloating tendency synthetic mica, the following compounds are mentioned suitably, for example. the Na tetra-chic mica NaMg_{2.5} (Si 4O10) -- F2, Na, or Li TENIO light (NaLi) Mg 2 (Si 4O10) -- F2, Na or Li hectorite (NaLi) / 3Mg₂/3Li1 / three (Si 4O10) F2, etc. is mentioned.

[0092] As size of said bloating tendency synthetic mica, thickness is 1-50nm and flat-surface size is 1-20 micrometers. It is so desirable that it is large in the range in which it is desirable and said flat-surface size, the more, does not get worse the smooth nature and transparency of a spreading side the more said

thickness is thin in respect of diffusion control. As an aspect ratio of said bloating tendency synthetic mica, it is usually 100 or more, and 200 or more are desirable and 500 or more are more desirable.

[0093] In order that thickening and gelation may progress by fixed solid content concentration (for example, 5 - 10%) if the ratio (1.5 to ten or more opposite gelatin) of a mica increases when said usual gelatin is used, it is necessary to lower viscosity. Although there is the approach of lowering concentration in order to lower this viscosity, as for lowering concentration, the desiccation load of a paint film will be increased, and the shape of a spreading side by impasto will get worse. Moreover, the approach of adding a urea, a salt, etc. in coating liquid, and the shape of a field after spreading is [a viscosity down is not fully obtained but] also bad. On the other hand, without producing such evil, said gelatin is the point that thickening and gelation can be reduced remarkably, and thickening and gelation can be remarkably reduced even if it uses it, mixing with a mica, and is advantageous.

[0094] As a content in said under coat of said water bloating tendency synthetic mica, $1/20$ - $1/2$ are desirable at the rate of a mass ratio of a mica/gelatin. When undercoat may stop fully functioning as an oxygen filter layer when the content of said water bloating tendency synthetic mica is less than $1/20$, and it exceeds one half, manufacture fitness, such as spreading nature, may get worse.

[0095] Moreover, as coverage of the mica in said undercoat, it is usually two or more [$0.01\text{g}/\text{m}^2$], and two or more $0.02\text{g}/\text{m}^2$ is desirable. Oxygen cutoff ability [in / that the coverage of said mica is less than two $0.01\text{g}/\text{m}^2$ / an under coat] may be unable to fall, and the property of preventing coloring of the natural complexion section etc. may be unable to be demonstrated.

[0096] (Interlayer) In this invention, when making said heat-sensitive recording layer into the laminated structure by the sensible-heat coloring layer from which a hue differs, it is desirable to prepare the interlayer for preventing color mixture etc. between each heat-sensitive recording layer. Although there is especially no limit and it can choose suitably as said interlayer according to the purpose, it can form using a water soluble polymer compound etc.

[0097] As said water soluble polymer compound, what consists of polyvinyl alcohol, denaturation polyvinyl alcohol, methyl cellulose, sodium polystyrene sulfonate, a styrene-maleic-acid copolymer, gelatin and/or a ZECHIRAN derivative, a polyethylene glycol, and/or a polyethylene-glycol derivative is mentioned suitably, for example.

[0098] Moreover, said interlayer can add said inorganic stratified compound suitably. If said interlayer contains said inorganic stratified compound, he can raise raw shelf life and color image shelf life by being able to prevent color mixture and controlling supply of oxygen by controlling and preventing the mass transfer between layers.

[0099] (Light transmittance adjustment layer) In this invention, a light transmittance adjustment layer can be prepared suitably. Said light transmittance adjustment layer has that desirable of preparing at least one layer into said thermal recording ingredient, and it is more desirable to form between said heat-sensitive recording layers and said protective layers. In addition, you may design so that said light transmittance adjustment layer may be used also [protective layer / said]. Since said light transmittance adjustment layer contains the component which functions as a precursor of an ultraviolet ray absorbent and it does not function as an ultraviolet ray absorbent before the optical exposure of the wavelength of a field required for fixing, light transmittance is high, in case said heat-sensitive recording layer is established, the wavelength of a field required for fixing is made to fully penetrate, and the permeability of a visible ray is also high, and trouble is not produced in fixing of said heat-sensitive recording layer.

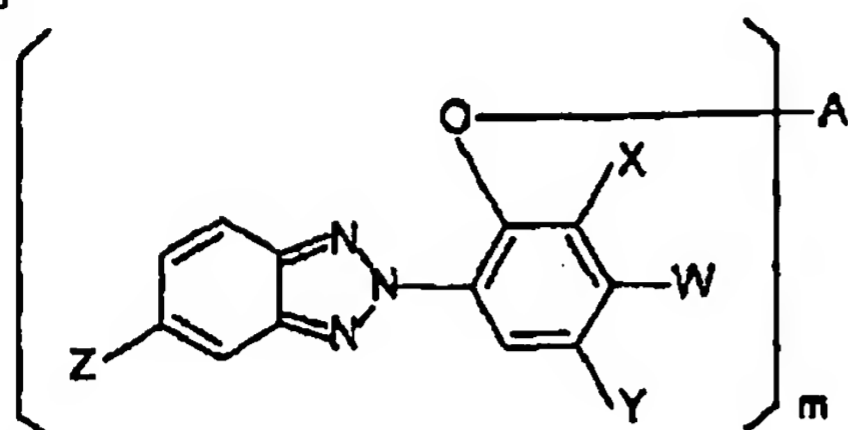
[0100] The component which functions as a precursor of said ultraviolet ray absorbent After the optical exposure of the wavelength of a field required for fixing by the optical exposure of said heat-sensitive recording layer is completed, Come to function as an ultraviolet ray absorbent by reacting with light or heat, and although the most is absorbed with an ultraviolet ray absorbent, permeability becomes low and the lightfastness of light of the wavelength of a field required for fixing of an ultraviolet-rays field of a thermal recording ingredient improves Since there is no absorption effect of a visible ray, the permeability of a visible ray does not change substantially.

[0101] As an example of the component which functions as a precursor of said ultraviolet ray absorbent, the compound expressed with either of following general formula (1) - (4) is mentioned suitably.

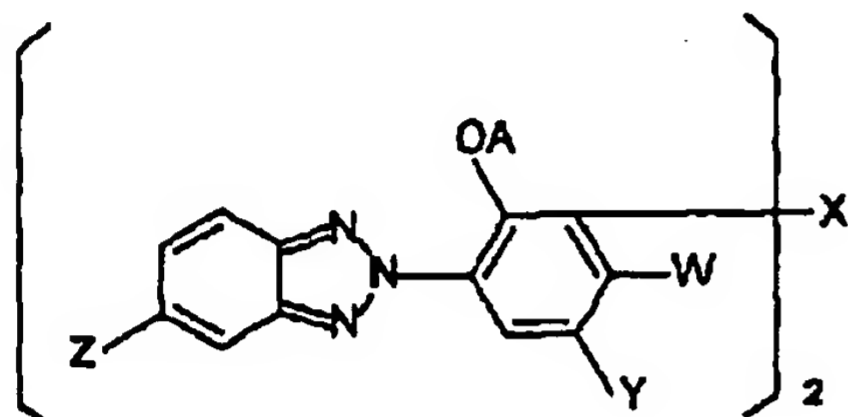
[0102]

[Formula 9]

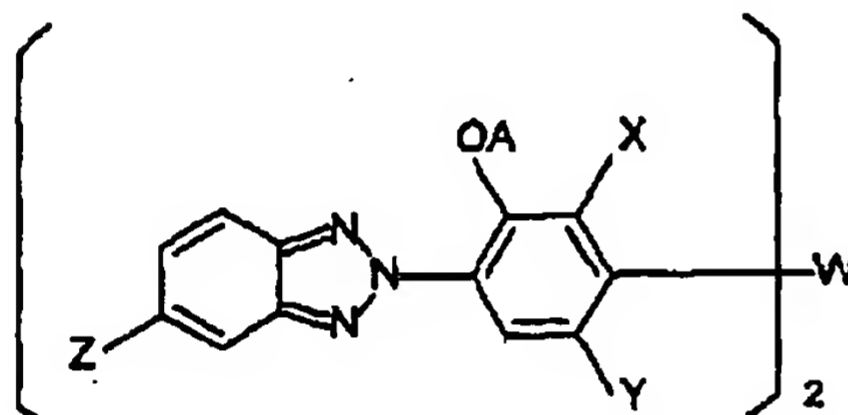
一般式 (1)



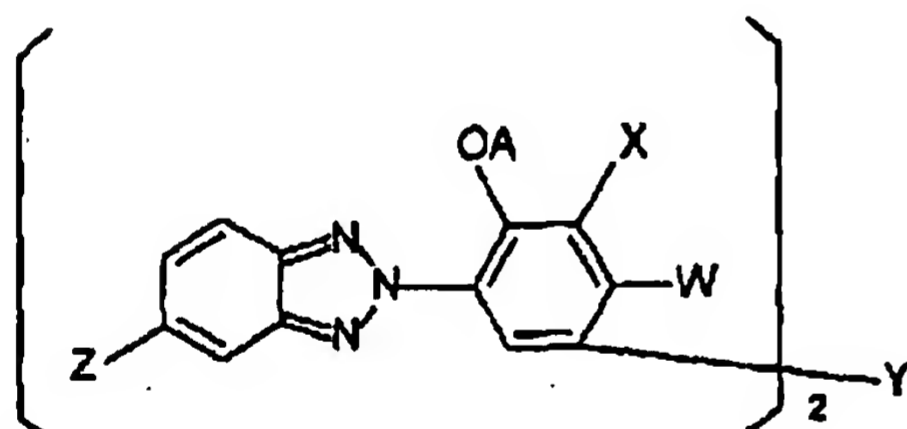
一般式 (2)



一般式 (3)



一般式 (4)



[0103] General formula (1) In - (4), m expresses 1 or 2. A expresses -SO₂-R, -CO-R, -CO₂-R, -CONH-R, -POR one R₂, -CH two R₃, or -SiR four R₅R₆ in the general formula at the time of m= 1 (1), and general formula (2) - (4). Moreover, A expresses -SO₂R₇SO₂-, -CO-, -COCO-, -COR₇CO-, -SO₂-, or -SO- in the general formula at the time of m= 2 (1).

[0104] X expresses a hydrogen atom, an alkyl group, an alkoxy group, an aryl group, or a halogen atom in a general formula (1), (3), and (4). Moreover, X expresses alkylene group and -OR₇O- or -OCOR₇CO₂- in a general formula (2). W expresses a hydrogen atom, an alkyl group, an alkoxy group, an aryl group, or a halogen atom in a general formula (1), (2), and (4). Moreover, W expresses -OR₇O- or -OCOR₇CO₂- in a general formula (3).

[0105] Y expresses a hydrogen atom, an alkyl group, an alkoxy group, an aryl group, or a halogen atom in a general formula (1), (2), and (3). Moreover, Y expresses -OR₇O-, -OCOR₇CO₂-, -CH₂CH₂CO₂R₇OCOCH₂CH₂-, -CH₂CH₂OCOR₇CO₂CH₂CH₂-, or -CH₂CH₂CON(R₈) R₇N(R₈) COCH₂CH₂- in a general formula (4).

[0106] Z expresses a hydrogen atom, a halogen atom, an alkyl group, or an alkoxy group. Here, R expresses an alkyl group or an aryl group. R₁ and R₂ express an alkoxy group, an aryloxy group, an alkyl group, or an aryl group. R₃ expresses the phenyl group permuted by the nitro group or at least one

methoxy group. R4, R5, and R6 express an alkyl group or an aryl group. R7 expresses an alkylene group or an arylene radical. R8 expresses a hydrogen atom or an alkyl group.

[0107] Said alkyl group may be a straight chain-like, and may be a letter of branching, and may have the unsaturated bond, and may be permuted by an alkoxy group, an aryloxy group, the alkoxy carbonyl group, the aryloxy carbonyl group, the aryl group, the hydroxy group, etc. Moreover, said aryl group may be further permuted by the alkyl group, the alkoxy group, or the halogen atom.

[0108] Said alkylene group may be a straight chain-like, may be a letter of branching, and may contain the unsaturated bond, the oxygen atom, the sulfur atom, and the nitrogen atom. Moreover, said alkylene group may be further permuted by the alkoxy group, the hydroxy group, the aryloxy group, or the aryl group.

[0109] Said arylene radical may be further permuted by the alkyl group, the alkoxy group, the halogen atom, etc.

[0110] As a substituent expressed with X, Y, and W, the alkyl group of carbon numbers 1-18, the alkoxy group of carbon numbers 1-18, the aryl group of carbon numbers 6-18, a fluorine atom, a chlorine atom, a bromine atom, or a hydrogen atom is desirable, and the alkyl group of carbon numbers 1-12, the alkoxy group of carbon numbers 1-12, a phenyl group or a hydrogen atom, and especially a chlorine atom are desirable also in these.

[0111] As a substituent expressed with Z, a hydrogen atom, a chlorine atom, a fluorine atom, the alkyl group of carbon numbers 1-12, and the alkoxy group of carbon numbers 1-12 are desirable, and the alkyl group of carbon numbers 1-6, the alkoxy group of carbon numbers 1-6 or a hydrogen atom, and especially a chlorine atom are desirable also in these.

[0112] As a substituent expressed with R, the alkyl group of carbon numbers 1-18 and the aryl group of carbon numbers 6-18 are desirable, and the alkyl group of carbon numbers 1-12 and especially the aryl group of carbon numbers 6-12 are desirable also in these.

[0113] As a substituent expressed with R1 and R2, the alkoxy group of carbon numbers 1-12, the aryloxy group of carbon numbers 6-12, the alkyl group of carbon numbers 1-12, and the aryl group of carbon numbers 6-12 are desirable.

[0114] As a substituent expressed with R3, 2-nitrophenyl group, 3, 5-dimethoxy phenyl group, 3 and 4, and 5-trimethoxyphenyl radical are desirable.

[0115] As a substituent expressed with R4, R5, and R6, the alkyl group of carbon numbers 1-12 or the aryl group of carbon numbers 6-12 is desirable, and especially the alkyl group or phenyl group of carbon numbers 1-8 is desirable.

[0116] As a substituent expressed with R7 to 1 intramolecular in the so-called bis-object which has two benzotriazol rings, the alkylene group of carbon numbers 1-12 or the arylene radical of carbon numbers 6-12 is desirable, and a hydrogen atom or the alkyl group of carbon numbers 1-6 is desirable as a substituent expressed with R8.

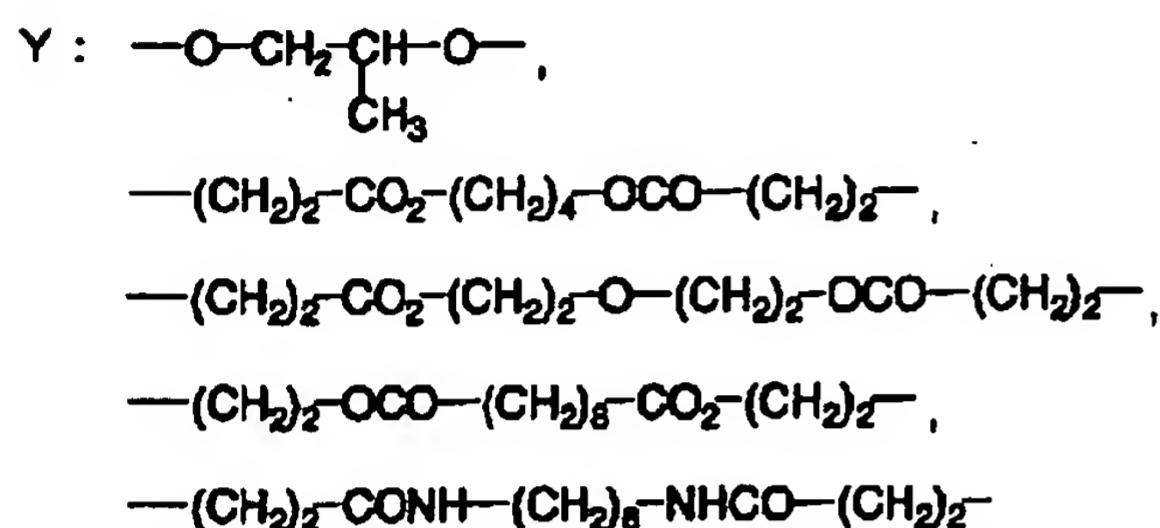
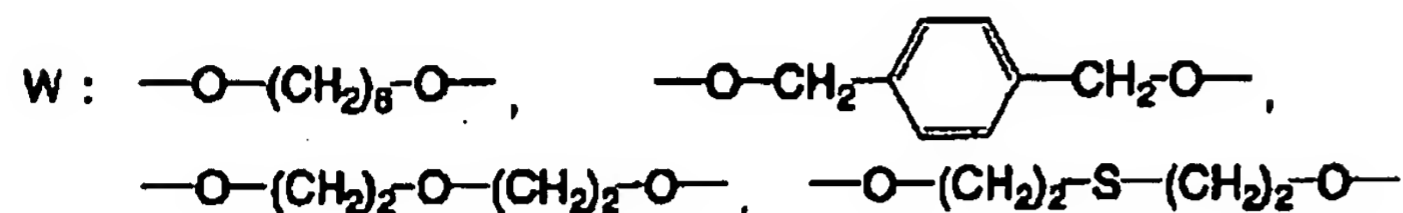
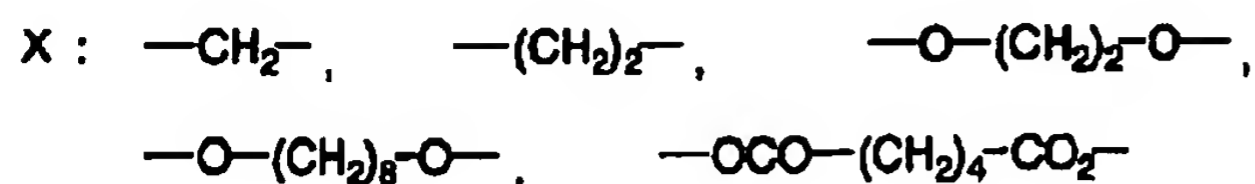
[0117] Especially as a substituent expressed with A, -SO₂R is desirable.

[0118] Hereafter, although the example of said substituent is given, this invention is not limited to this.

As a univalent thing, among the substituents expressed with X, Y, and W A hydrogen atom, a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, a pentyl radical, A hexyl group, an octyl radical, a decyl group, the dodecyl, an allyl group, 2-butenyl group, Benzyl, alpha-dimethylbenzyl radical, a methoxy group, an ethoxy radical, a propyloxy radical, A butyloxy radical, an octyloxy radical, a dodecyloxy radical, a methoxyethoxy radical, A phenoxy ethoxy radical, a methoxy carbonylethyl radical, an ethoxy carbonylethyl radical, A propyloxy carbonylethyl radical, a butyloxy carbonylethyl radical, An octyloxy carbonylethyl radical, a phenoxy carbonylethyl radical, a phenyl group, a tolyl group, a chlorine atom, a fluorine atom, a bromine atom, etc. are mentioned, and the following are mentioned as a divalent thing.

[0119]

[Formula 10]

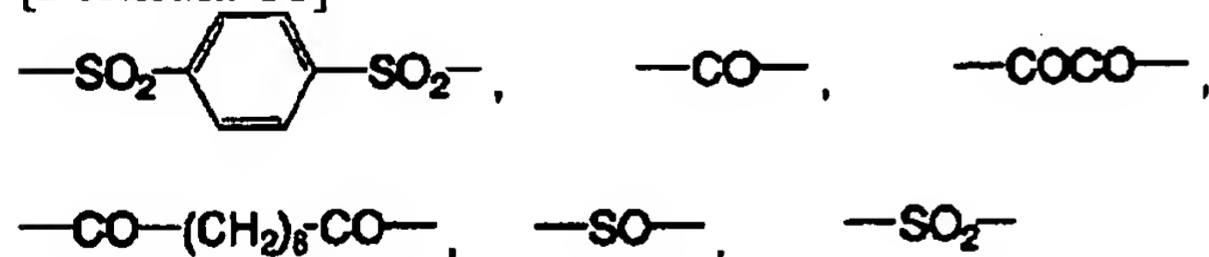


[0120] As a substituent expressed with Z, a hydrogen atom, a chlorine atom, a methyl group, an ethyl group, a propyl group, a hexyl group, a methoxy group, an ethoxy radical, a propyloxy radical, an octyloxy radical, etc. are mentioned.

[0121] As a univalent thing, as a substituent expressed with A A methane sulfonyl group, an ethane sulfonyl group, a butane sulfonyl group, a benzenesulphonyl radical, 4-methylbenzene sulfonyl group, 2-mesitylene sulfonyl group, 4-methoxybenzene sulfonyl group, 4-octyloxy benzenesulphonyl radical, 2 and 4, 6-triisopropyl benzenesulphonyl radical, beta-styrene sulfonyl group, a vinylbenzene sulfonyl group, 4-chlorobenzene sulfonyl group, 2, 5-dichlorobenzene sulfonyl group, 2 and 4, 5-trichlorobenzene sulfonyl group, A 1-naphthalene sulfonyl group, 2-naphthalene sulfonyl group, a quinoline sulfonyl group, A thiophene sulfonyl group, an acetyl group, a propionyl radical, a butyryl radical, A pivaloyl radical, a lauroyl radical, a stearoyl radical, benzoyl, a cinnamoyl radical, A furoyl radical, a nicotinoyl group, a methoxycarbonyl group, an ethoxycarbonyl radical, A phenoxy carbonyl group, a hexylamino carbonyl group, a phenylaminocarbonyl radical, A diphenyl phosphoryl group, a diethyl phosphoryl group, 2-nitrobenzyl radical, 3, 5-dimethoxy benzyl, 3 and 4, 5-trimethoxy benzyl, A trimethylsilyl radical, a triethyl silyl radical, t-butyl dimethylsilyl radical, a diethyl isopropyl silyl radical, a dimethylphenyl silyl radical, a diphenyl methyl silyl radical, a triphenyl silyl radical, etc. are mentioned, and the following are mentioned as a divalent thing.

[0122]

[Formula 11]



[0123] When A is -SiR four R5R6, photo-oxide generating agents, such as ammonium salt, diazonium salt, iodonium salt, sulfonium salt, phosphonium salt, and an onium salt, may be used together for the purpose of improvement in photoreaction nature. as the example of these photo-oxide generating agents -- "imaging -- business -- the thing of a publication is mentioned to organic material" (the volume on organic electronics ingredient study group, 1993).

[0124] Said general formula (1) The compound expressed with - (4) is simply compoundable by the well-known approach conventionally, and these may be used by the one-sort independent and may use two or more sorts together.

[0125] About the mode of the content of a compound expressed with said general formula (1) - (4) in said light transmittance adjustment layer There is especially no limit and it can be suitably chosen according to the purpose. For example, these (-- one --) -- a solid-state -- distribution -- depending -- containing -- making -- an approach -- (-- two --) -- emulsification -- distribution -- containing -- making -- an approach -- (-- three --) -- a polymer -- distribution -- containing -- making -- an approach -- (-- four --) -- a latex -- distribution -- containing -- making -- an approach -- (-- five --) -- microencapsulation -- carrying out -- containing -- making -- an approach -- etc. -- mentioning -- having . Also in these, the approach of making it contain by emulsification distribution and the approach of making it microencapsulate and contain are desirable.

[0126] As the approach of said emulsification distribution, the compound first expressed with said general formula (1) - (4) is dissolved in oil. this oil -- ordinary temperature -- a solid-state -- you may be -- a liquid -- you may be -- a polymer -- you may be -- low-boiling point auxiliary solvents, such as acetic ester, a methylene chloride, and a cyclohexanone, and/-- the acid ester which is not stretched again, phthalic ester, acrylic ester, methacrylic ester, other carboxylic-acid ETESURU, a fatty-acid amide, an alkylation biphenyl, alkylation terphenyl, alkylation naphthalene, diaryl ethane, chlorinated paraffin, an alcoholic system, a phenol system, an ether system, a monoolefin system, an epoxy system, etc. are mentioned.

[0127] As an example, phosphoric acid TORIKUREJIRU, phosphoric acid trioctyl, phosphoric acid octyl diphenyl, Phosphoric acid tricyclohexyl, dibutyl phthalate, a dioctyl phthalate, A phthalic-acid JIRAU rate, dicyclohexyl phthalate, olefin acid butyl, Diethylene-glycol benzoate, a dioctyl sebacate, a dibutyl sebacate, Dioctyl adipate, trimellitic acid trioctyl, acetyl triethyl citrate, Maleic-acid octyl, dibutyl maleate, an isoamyl biphenyl, Chlorinated paraffin, diisopropyl naphthalene, 1, 1'-JITORIRU ethane, High-boiling point oil, such as 2, 4-JITA-Shari p tert amylphenol, N, an N-dibutyl-2-butoxy-5-tertiary octyl aniline, hydroxybenzoic-acid 2-ethylhexyl ester, and a polyethylene glycol, etc. is mentioned. These may be used by the one-sort independent, and may use two or more sorts together, and an alcoholic system, a phosphoric ester system, a carboxylic-acid system ester system, an alkylation biphenyl, alkylation terphenyl, alkylation naphthalene, and diaryl ethane are desirable also in these.

[0128] In this invention, carbonization inhibitors, such as a hindered phenol and hindered amine, may be added in said oil. Said general formula (1) It adds in the water solution of a water soluble polymer, and emulsification distribution of said oil containing the compound expressed with - (4) is carried out with a colloid mill, a homogenizer, or a supersonic wave.

[0129] As said water soluble polymer, polyvinyl alcohol, silanol denaturation polyvinyl alcohol, carboxy denaturation polyvinyl alcohol, amino denaturation polyvinyl alcohol, itaconic-acid denaturation polyvinyl alcohol, a styrene maleic-anhydride copolymer, a butadiene maleic-anhydride copolymer, an ethylene maleic-anhydride copolymer, an isobutylene maleic-anhydride copolymer, polyacrylamide, polystyrene sulfonate, a polyvinyl pyrrolidone, an ethylene-acrylic-acid copolymer, gelatin, etc. are mentioned. In this invention, a surface active agent etc. may be added to said water soluble polymer if needed, and an emulsion or a latex of a hydrophobic giant molecule etc. may be used together.

[0130] When microencapsulating said diazonium salt compound or the compound expressed with said general formula (1) - (4), as the approach of the microencapsulation, a well-known approach can be used conventionally. For example, said diazonium salt compound or the compound expressed with said general formula (1) - (4), A microcapsule wall precursor is dissolved in an organic solvent refractory in water, or insoluble. The high polymer which carries out emulsification distribution using a homogenizer etc. by adding in the water solution of a water soluble polymer, carries out a temperature up, and serves as a microcapsule wall by forming wall membrane in an oil / water interface The microcapsule of this diazonium salt compound or the compound expressed with this general formula (1) - (4) can be prepared.

[0131] As an example of said microcapsule wall membrane, the wall membrane which consists of polyurethane resin, polyurea resin, polyamide resin, polyester resin, polycarbonate resin, amino aldehyde resin, melamine resin, polystyrene resin, the styrene acrylate copolymer resin, the styrene

methacrylate copolymer resin, gelatin, polyvinyl alcohol, etc. is mentioned, for example. Also in these, the wall membrane which consists of polyurethane polyurea resin is desirable.

[0132] The microcapsule which has wall membrane which consists of this polyurethane polyurea resin mixes microcapsule wall precursors, such as for example, multiple-valued isocyanate, in the heart matter which should microencapsulate, carries out emulsification distribution at the water solution of water soluble polymers, such as polyvinyl alcohol, and is manufactured by raising solution temperature and causing a macromolecule formation reaction by the oil droplet interface.

[0133] As an example of said multiple-valued isocyanate compound m-phenylene diisocyanate, p-phenylene diisocyanate, 2, 6-tolylene diisocyanate, 2, 4-tolylene diisocyanate, Naphthalene -1, 4-diisocyanate, diphenylmethane-4,4'-diisocyanate, 3 and 3'-diphenylmethane-4,4'-diisocyanate, a xylene -1, 4-diisocyanate, 4 and 4'-diphenylpropanediisocyanate, trimethylene diisocyanate, Hexamethylene diisocyanate, a propylene -1, 2-diisocyanate, A butylene -1, 2-diisocyanate, the cyclo hexylene -1, 2-diisocyanate, Diisocyanate, such as the cyclo hexylene -1 and 4-diisocyanate Tri-isocyanate, such as 4, 4', 4"-triphenylmethane triisocyanate, and toluene-2,4,6-triisocyanate Tetra-isocyanates, such as 4 and 4'-dimethyl diphenylmethane -2, 2', 5, and 5'-tetra-isocyanate The addition product of hexamethylene diisocyanate and trimethylol propane, Isocyanate prepolymers, such as an addition product of 2 and 4-tolylene diisocyanate and trimethylol propane, an addition product of xylylene diisocyanate and trimethylol propane, and an addition product of tolylene diisocyanate and hexane triol, etc. are mentioned. These have especially the desirable thing that may use it by the one-sort independent, may use two or more sorts together, and has three or more isocyanate radicals in intramolecular also in these.

[0134] In the approach of said microencapsulation, the oil shown in the approach of said emulsification distribution as an organic solvent in which said diazonium salt compound or the compound expressed with said general formula (1) - (4) is dissolved can be used. Moreover, the same is said of a water soluble polymer.

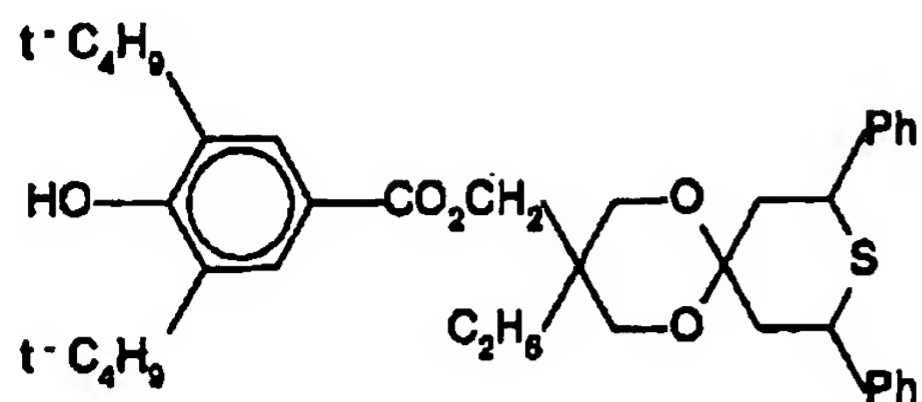
[0135] As mean particle diameter of said microcapsule, 0.1-1.0 micrometers is desirable and 0.2-0.7 micrometers is more desirable.

[0136] In this invention, since lightfastness is raised further, the well-known antioxidant shown below can be added in said thermal recording ingredient. As such an antioxidant, for example The Europe public presentation patent No. 310551 official report, The German public presentation patent No. 3435443 official report, the Europe public presentation patent No. 310552 official report, JP,3-121449,A, the Europe public presentation patent No. 459416 official report, JP,2-262654,A, JP,2-71262,A, JP,63-163351,A, The U.S. patent No. 4814262, JP,54-48535,A, JP,5-61166,A, JP,5-119449,A, the U.S. patent No. 4980275, JP,63-113536,A, JP,62-262047,A, The antioxidant of a publication etc. is mentioned to the Europe public presentation patent No. 223739 official report, the Europe public presentation patent No. 309402 official report, the Europe public presentation patent No. 309401 official report, etc., and, specifically, the following are mentioned.

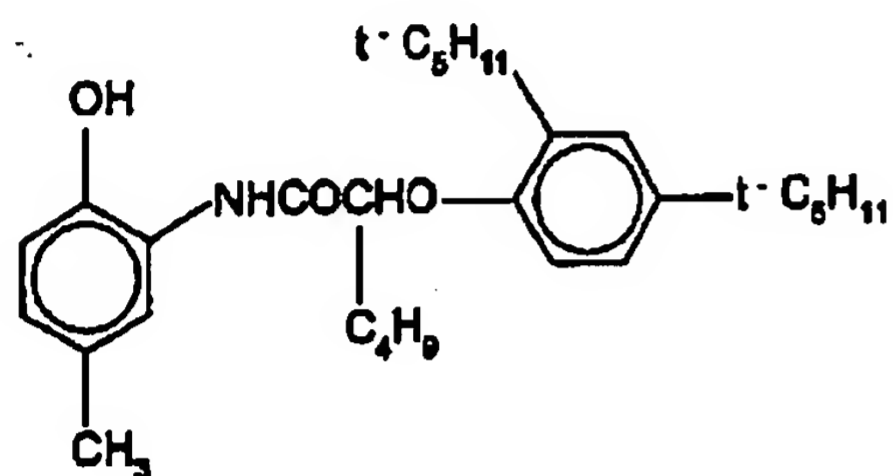
[0137]

[Formula 12]

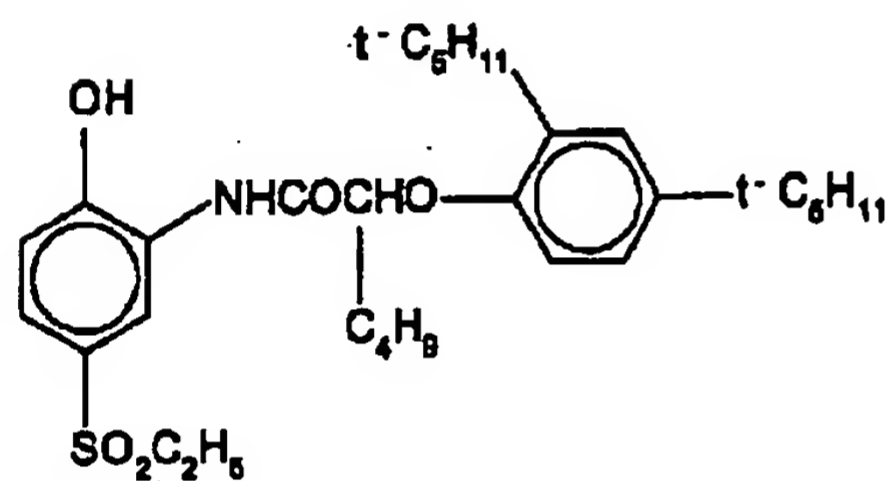
Q-1



Q-2



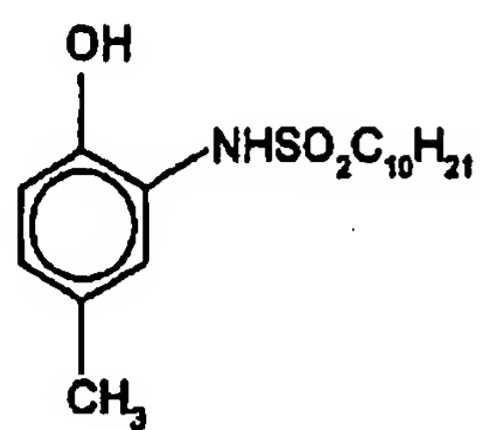
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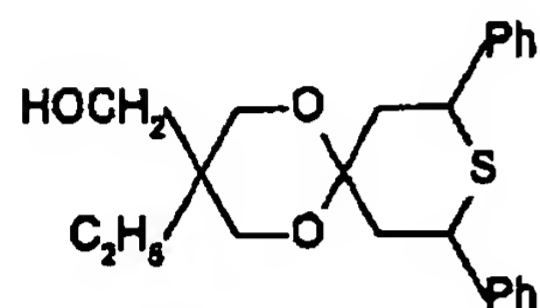
[0138]

[Formula 13]

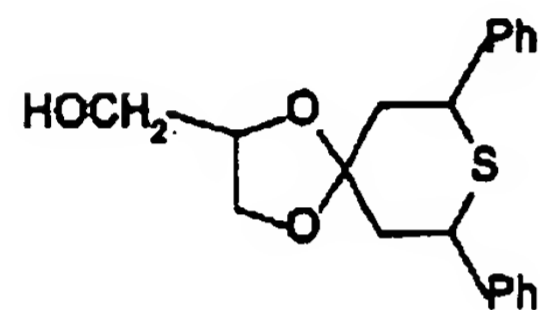
Q-4



Q-5



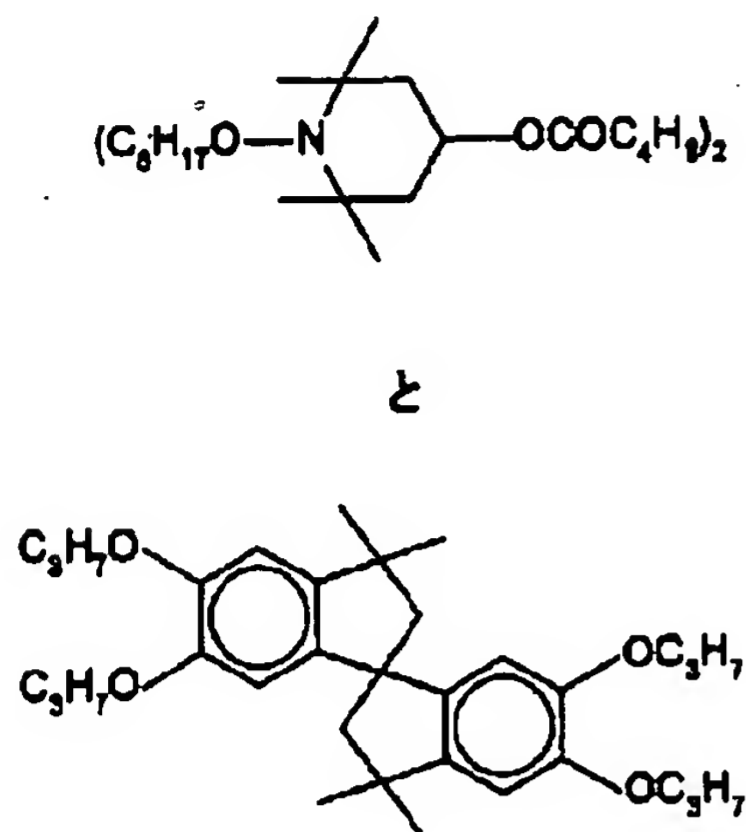
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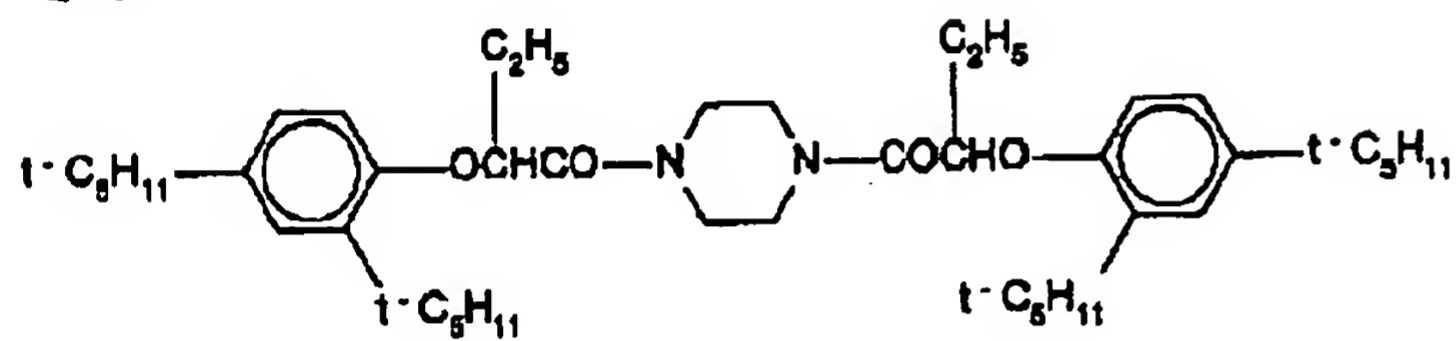
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[Formula 14]

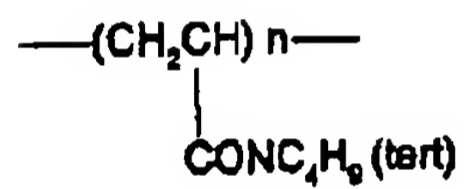
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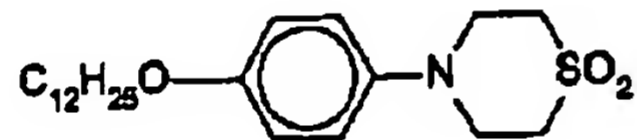
Q-8



Q-9



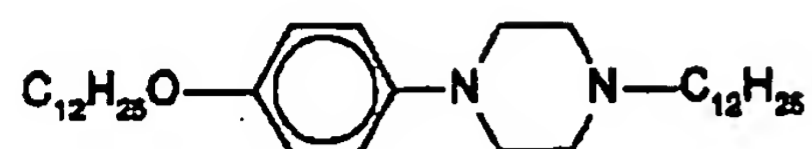
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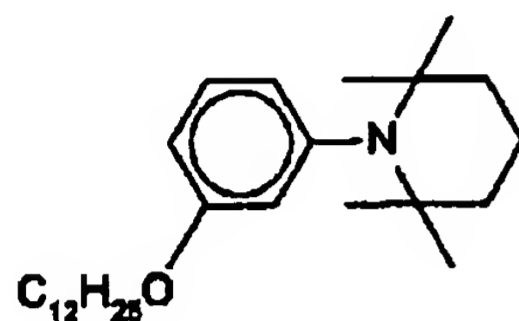
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[Formula 15]

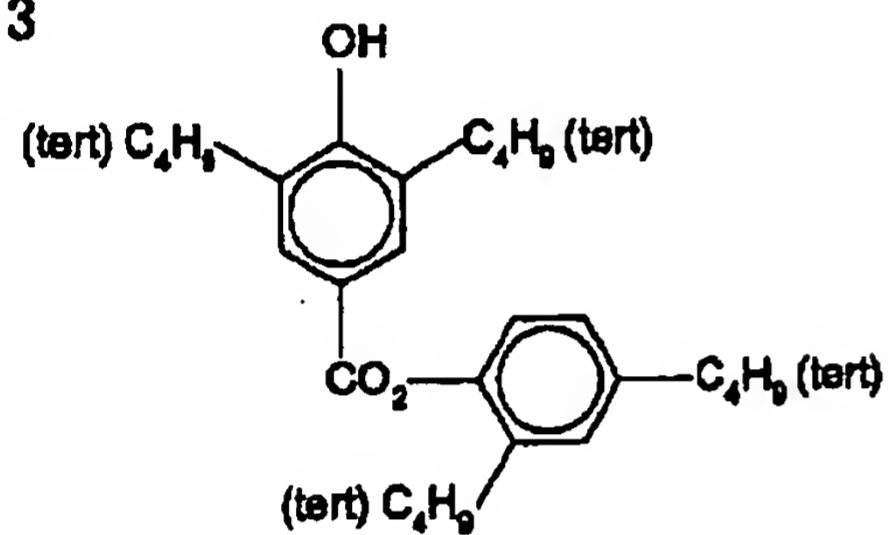
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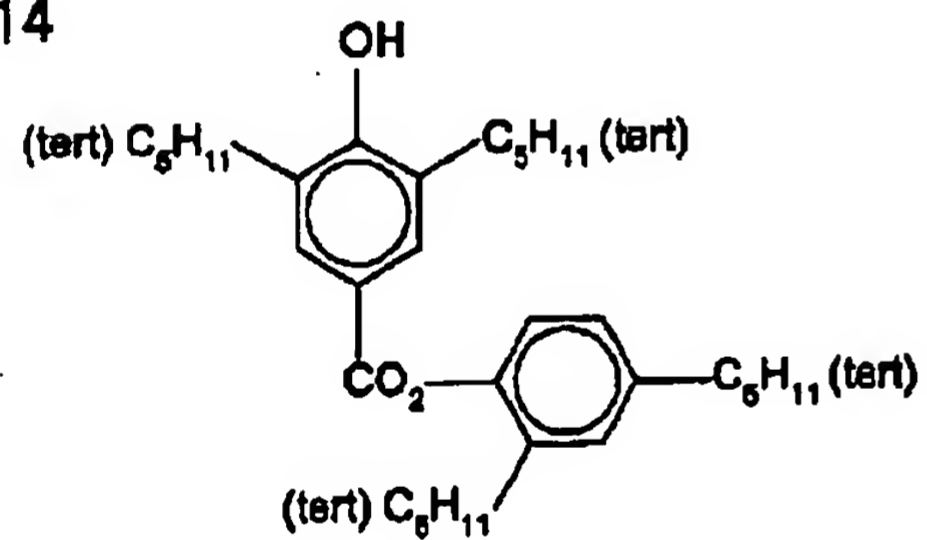
Q-12



Q-13



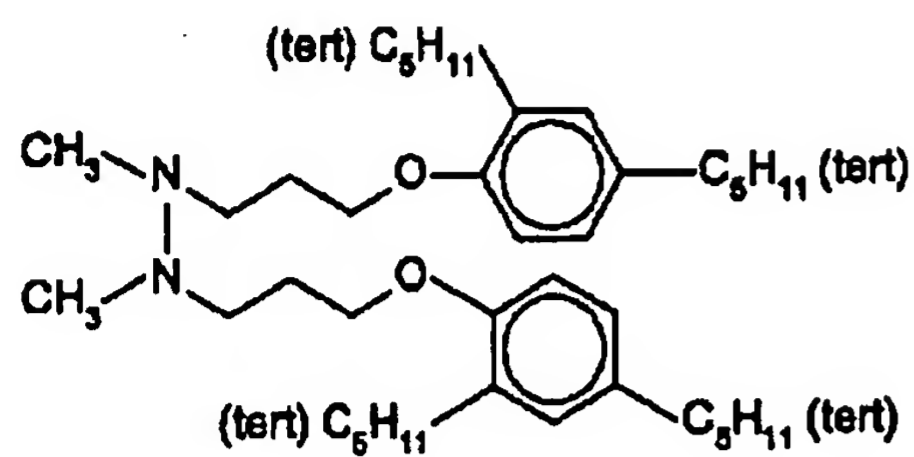
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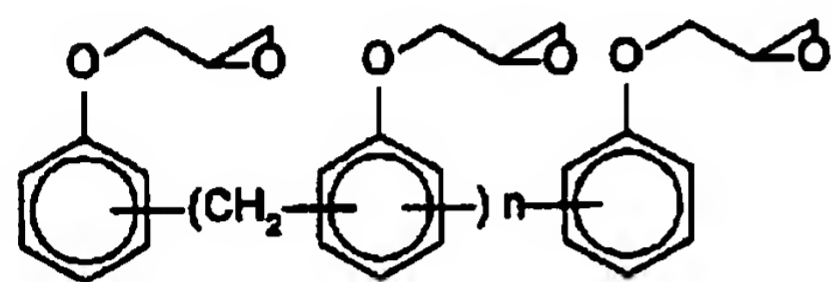
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[Formula 16]

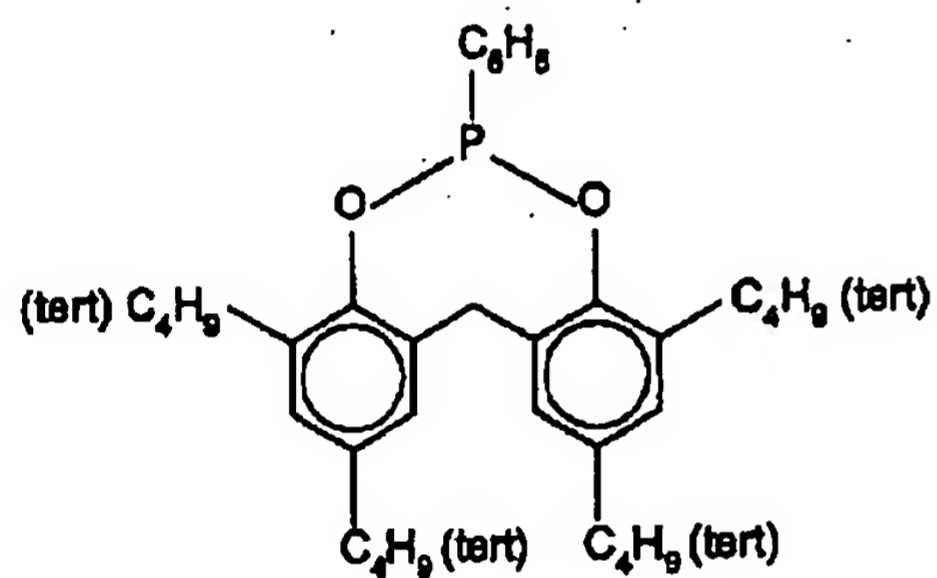
Q-15



Q-16



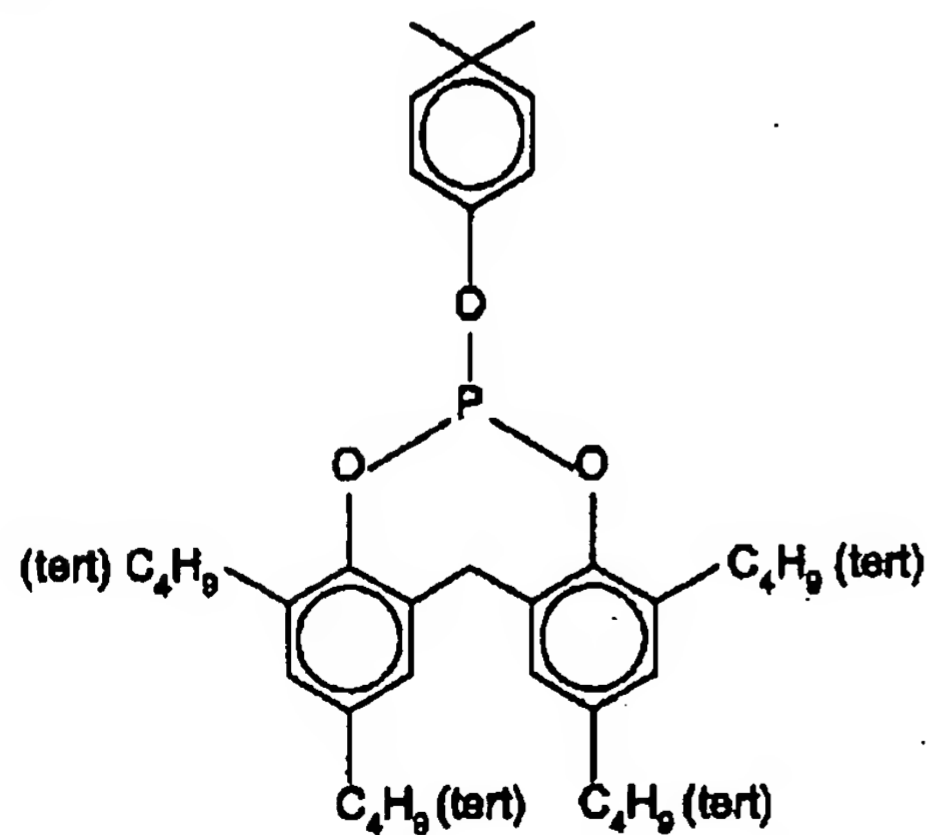
Q-17



[0142]

[Formula 17]

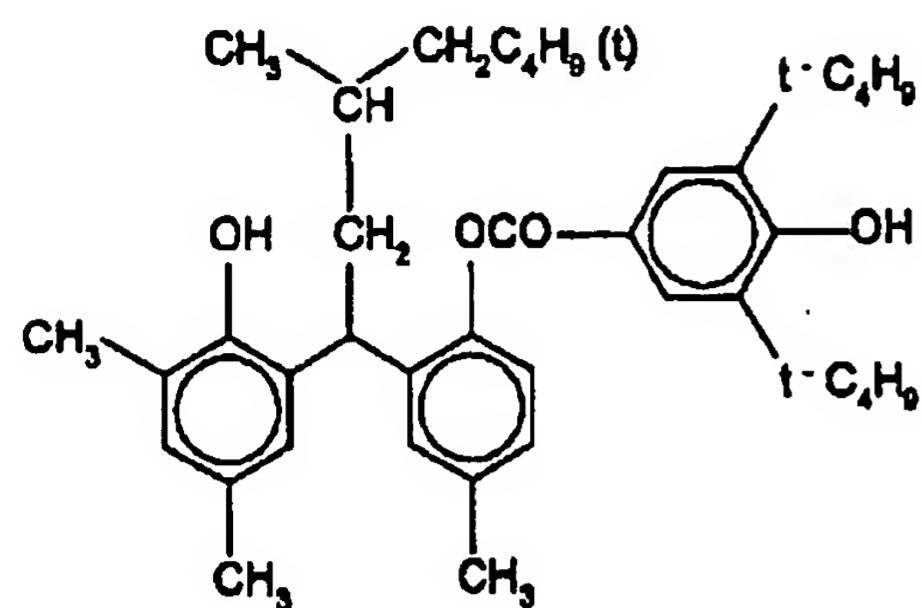
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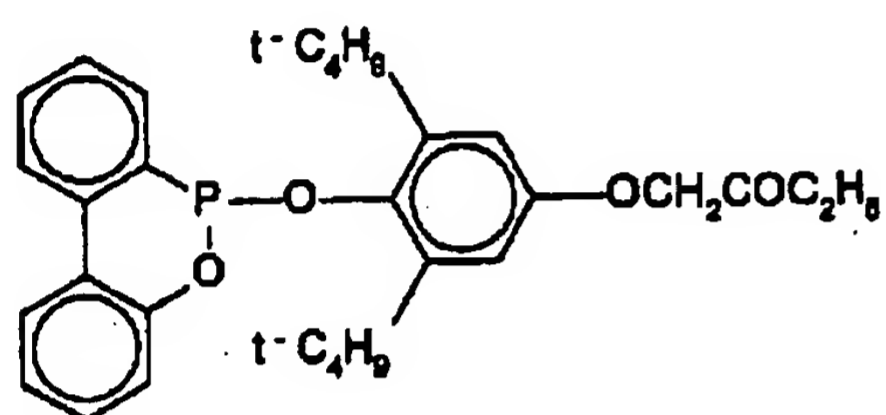
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[Formula 18]

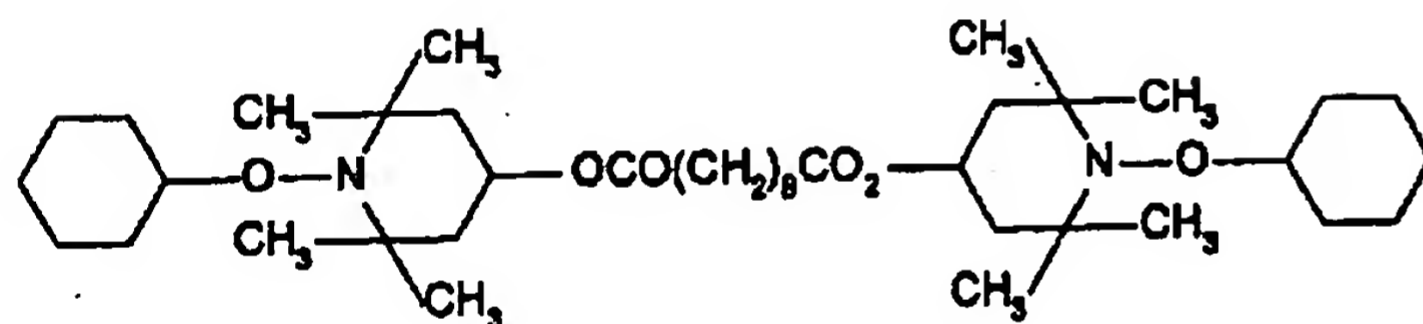
Q-19



Q-20

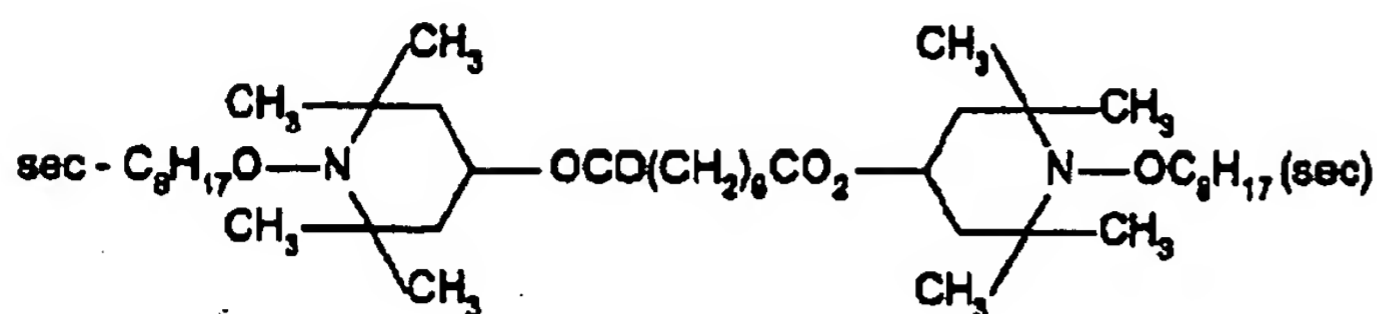


Q-21

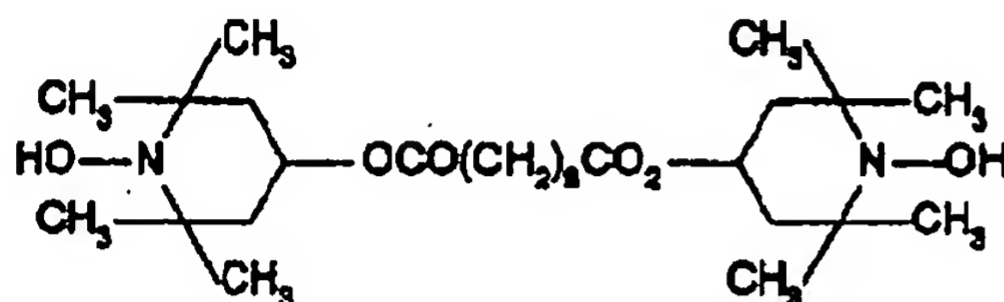


[0144]
[Formula 19]

Q-22



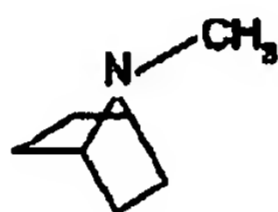
Q-23



Q-24



Q-25



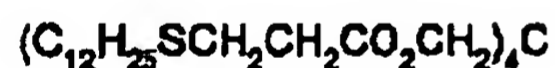
Q-26



Q-27



Q-28



[0145] Moreover, JP,60-125470,A, JP,60-125471,A, JP,60-125472,A, JP,60-287485,A, JP,60-287486,A, JP,60-287487,A, JP,62-146680,A, JP,60-287488,A, JP,62-282885,A, JP,63-89877,A, JP,63-88380,A, JP,63-088381,A, JP,01-239282,A, JP,04-291685,A, JP,04-291684,A, JP,05-188687,A, JP,05-188686,A, JP,05-110490,A, JP,05-1108437,A, JP,05-170361,A, JP,63-203372,A, JP,63-224989,A, JP,63-267594,A, JP,63-182484,A, JP,60-107384,A, JP,60-107383,A, JP,61-160287,A, JP,61-185483,A, The antioxidant of a publication is mentioned to JP,61-211079,A, JP,63-251282,A, JP,63-051174,A, JP,48-043294,B, JP,48-033212,B, etc.

[0146] In an example, it is 6-ethoxy-1-phenyl - 2, 2, 4-trimethyl -1, a 2-dihydroquinoline, 6-ethoxy-1-octyl - 2, 2, 4-trimethyl -1, a 2-dihydroquinoline, 6-ethoxy-1-phenyl - 2, 2, 4-trimethyl -1, 2, 3, 4-tetrahydroquinoline, 6-ethoxy-1-octyl - 2, 2, 4-trimethyl -1, 2, 3, 4-tetrahydroquinoline, A cyclohexane acid nickel, 2, and 2-bis--4-hydroxyphenyl propane, 1, and 1-bis--4-hydroxyphenyl-2-ethyl hexane, 2-methyl-4-methoxy diphenylamine, 1-methyl-2-phenylindole, etc. are mentioned. These antioxidants can be added to said heat-sensitive recording layer, said interlayer, said light transmittance adjustment layer, and said protective layer.

[0147]

[Example] Although the example of this invention is explained below, this invention is not limited to these examples at all. In addition, unless the "section" has a notice especially in below, the "mass

section" is meant altogether.

[0148] (Example 1)

The preparation-zymolysis gelatin (viscosity: 10000 average molecular weight : PAGI law 15 mP, PAGI law jelly strength : 20g) 40 section of a <under coat>-gelatin solution was added to the water 60 section, the stirring dissolution was carried out at 40 degrees C, and the gelatin solution was prepared.

After mixing the synthetic mica (aspect ratio: 1000, trade name SOMASHIFU ME 100, CO-OP CHEMICAL CO., LTD. make) 8 section of the preparation-water bloating tendency of - mica dispersion liquid, and the water 92 section, wet distribution was carried out by bis-KOMIRU, and the mica dispersion liquid whose mean particle diameter is 2.0 micrometers were obtained. Water was added so that mica concentration might become these mica dispersion liquid with 5 mass %, and it mixed to homogeneity, and desired mica dispersion liquid were prepared.

[0149] Formation of - under coat - The 5 mass % aforementioned mica dispersion-liquid 208 section was added, after adding the water 120 section and the methanol 556 section and carrying out stirring mixing enough, stirring mixing was carried out enough and the 1.66 mass % ethyleneoxide system surfactant 9.8 section was added to the 40 mass % aforementioned gelatin solution 100 40-degree C section. And solution temperature was kept at 40 degrees C from 35 degrees C, the gelatin hardening agent 7.3 section expressed with said E-1 was added, and the coating liquid for under coats (5.7 mass %) was prepared.

[0150] This coating liquid for under coats was applied on the base material which laminates polyester film to both sides of paper of fine quality, and becomes them so that the coverage of a mica may serve as 0.2 g/m², and the under coat was formed.

[0151] As a preparation-electron-donative colorlessness color precursor of <preparation of coating liquid for heat-sensitive recording layer A>-electron-donative colorlessness color precursor microcapsule liquid, the crystal violet lactone 3.0 section was dissolved in the ethyl-acetate 20 section, and the 20 sections added, the alkyl naphthalene which is a high-boiling point solvent further was heated, and it mixed to homogeneity. As a microcapsule wall agent, the xylylene diisocyanate / trimethylol propane addition product 20 section was further added in this solution, it stirred to homogeneity, and this was made into the electron-donative colorlessness color precursor solution. Separately, the 6 mass % water-solution 54 section of gelatin was prepared, said electron-donative colorlessness color precursor solution was added, and emulsification distribution was carried out with the homogenizer. After adding the water 68 section to the obtained emulsified liquid and equalizing, carried out the temperature up to 50 degrees C, stirring, the microencapsulation reaction was made to perform for 3 hours, and electron-donative colorlessness color precursor microcapsule liquid was prepared. The mean particle diameter of a microcapsule was 1.6 micrometers.

[0152] The bisphenol A 30 section was added into the gelatin 4 mass % water-solution 150 section as a preparation-electronic receptiveness compound of - electronic receptiveness compound dispersion liquid, the ball mill distributed for 24 hours, and electronic receptiveness compound dispersion liquid were obtained. The mean particle diameter of said electronic receptiveness compound in these electronic receptiveness compound dispersion liquid was 1.2 micrometers.

[0153] Preparation -, next said electron-donative color precursor microcapsule liquid of the coating liquid for - heat-sensitive recording layer A, Said electronic receptiveness compound dispersion liquid are mixed so that the ratio of an electron-donative color precursor / electronic receptiveness compound may become 1/2. Furthermore, sodium dodecylbenzenesulfonate expressed with said structure expression (1) was added so that the coverage in the heat-sensitive recording layer A which applied and formed this coating liquid for heat-sensitive recording layer A might serve as 0.1 g/m², and the target coating liquid for heat-sensitive recording layer A was prepared.

[0154] It is 4 as a preparation-diazonium salt compound of <preparation of coating liquid for heat-sensitive recording layer B>-diazonium salt compound microcapsule liquid. - (the N-(2-(2, 4-G tert-amyl phenoxy) butyryl) PIPERAJINOBENZEN diazonium hexafluoro phosphate 2.0 section was dissolved in the ethyl-acetate 20 section, the 20 sections added, the alkyl naphthalene which is a high **** solvent further was heated, and it mixed to homogeneity.) As a microcapsule wall agent, the

xylylene diisocyanate / trimethylol propane addition product 15 section was further added in this solution, and it stirred to homogeneity. Separately, the 6 mass % water-solution 54 section of gelatin was prepared, the previous diazonium salt compound solution was added, and emulsification distribution was carried out with the homogenizer. After adding the water 68 section to the obtained emulsified liquid and equalizing, carried out the temperature up to 40 degrees C, stirring, the microencapsulation reaction was made to perform for 3 hours, and target diazonium salt compound microcapsule liquid was prepared. The mean particle diameter of a microcapsule was 1.1 micrometers. [0155] As a preparation-coupler of - coupler emulsified liquid, the 1-(2'-octyl phenyl)-3-methyl-5-pyrazolone 2 section, The 1, 2, and 3-triphenyl guanidine 2 section, 1, the 1-(p-hydroxyphenyl)-2-ethyl hexane 2 section, The 4 and 4'-(p-phenylene diisopropylidene) diphenol 4 section, The 2-ethylhexyl-4-hydroxy benzoate 4 section, the tricresyl phosphate 0.3 section, The diethyl-maleate 0.1 section and the 70% calcium dodecylbenzenesulfonate methanol solution 1 section After having dissolved into the ethyl-acetate 10 section, adding this solution in the gelatin water-solution 80 section 8% and emulsifying for 10 minutes with a homogenizer, ethyl acetate was removed and target coupler emulsified liquid was prepared.

[0156] Preparation - next said diazonium salt compound microcapsule liquid, and said coupler dispersion liquid of the coating liquid for - heat-sensitive recording layer B were mixed so that the ratio of a diazonium salt compound / coupler might be set to two thirds, and the target coating liquid for heat-sensitive recording layer B was prepared.

[0157] The 2 and 5-dibutoxy-4-TORIRUCHIOBENZEN diazonium hexafluoro phosphate 3.0 section was dissolved in the ethyl-acetate 20 section as a preparation-diazonium salt compound of <coating liquid for heat-sensitive recording layer C>-diazonium salt compound microcapsule liquid, the 20 sections added, the alkyl naphthalene which is a high-boiling point solvent further was heated, and it mixed to homogeneity. As a microcapsule wall agent, the xylylene diisocyanate / trimethylol propane addition product 15 section was further added in this solution, and it stirred to homogeneity. Separately, the 6 mass % water-solution 54 section of gelatin was prepared, the previous diazonium salt compound solution was added, and emulsification distribution was carried out with the homogenizer. After adding the water 68 section to the obtained emulsified liquid and equalizing, carried out the temperature up to 40 degrees C, stirring, the microencapsulation reaction was made to perform for 3 hours, and target diazonium salt compound microcapsule liquid was obtained. The mean particle diameter of a microcapsule was 1.0 micrometers.

[0158] As a preparation-coupler of - coupler dispersion liquid, the 2-chloro-5-(3-(2, 4-G tert-pentyl) phenoxy propylamino) acetoacetanilide 2 section, The 1, 2, and 3-triphenyl guanidine 2 section, 1, the 1-(p-hydroxyphenyl)-2-ethyl hexane 2 section, The 4 and 4'-(p-phenylene diisopropylidene) diphenol 4 section, The 2-ethylhexyl-4-hydroxy benzoate 4 section, the tricresyl phosphate 0.3 section, The diethyl-maleate 0.1 section and the 70% DOTESHIRU benzenesulfonic acid calcium methanol solution 1 section After having dissolved into the ethyl-acetate 10 section, adding this solution in the gelatin water-solution 80 section 8% and emulsifying for 10 minutes with a homogenizer, ethyl acetate was removed and target coupler dispersion liquid were prepared.

[0159] Preparation - next said diazonium salt compound microcapsule liquid, and said coupler dispersion liquid of the coating liquid for - heat-sensitive recording layer C were mixed so that the ratio of a diazonium salt compound / coupler might be set to four fifths, and the target coating liquid for heat-sensitive recording layer C was prepared.

[0160] The [2-allyl compound-6-(2H-benzotriazol-2-IRU)-4-t-octyl phenyl] benzene sulfonate 10 section, 2, the 5-G t-octyl-hydroquinone 3 section, the tricresyl phosphate 2 section, and the alpha-methyl-styrene dimer 4 section were dissolved in the preparation-ethyl-acetate 30 section of <light transmittance adjustment layer>-ultraviolet ray absorbent precursor microcapsule liquid as an ultraviolet ray absorbent precursor. As a microcapsule wall agent, the xylylene diisocyanate / trimethylol propane addition product 20 section was further added in this solution, and it stirred to homogeneity. Separately, the itaconic-acid denaturation polyvinyl alcohol 8% water-solution 200 section was prepared, the previous ultraviolet ray absorbent precursor solution was added, and emulsification distribution was

carried out with the homogenizer. Stirring, after adding the water 120 section to the obtained emulsified liquid and equalizing, carried out the temperature up to 40 degrees C, the capsulation reaction was made to perform for 3 hours, and target ultraviolet ray absorbent precursor microcapsule liquid was prepared. The mean particle diameter of a microcapsule was 0.3 micrometers.

[0161] Preparation of the coating liquid for - light transmittance adjustment layers - The [4-nonyl phenoxy trioxyethylene] butyl sulfonic-acid sodium water-solution 10 section was added 2% in said ultraviolet ray absorbent precursor microcapsule liquid 100 section, and the coating liquid for light transmittance adjustment layers was prepared in it.

[0162] In the gelatin water-solution 100 section, the butyl sulfonic-acid sodium 2 section was added 2% (4-nonyl phenoxy trioxyethylene) <preparation of coating liquid for the middle class> 10%, and the coating liquid for the middle class was prepared.

[0163] The anion nature special polycarboxylic acid mold macromolecule activator (trade name: poise 532A (40 mass % water solution), Kao Corp. make) 0.1 section and the ion-exchange-water 15.9 section were mixed in the production-barium-sulfate (trade name: BF-21F, Sakai Chemical Industry Co., Ltd. make) 4 section of the pigment distribution object for <preparation of coating liquid for protective layers>-protective layers, it distributed in dynamill, and barium-sulfate dispersion liquid were produced. These dispersion liquid were 0.15 micrometers or less in the median size as a result of particle-size measurement (it carries out by LA-910 and the Horiba, Ltd. make). To the barium-sulfate dispersion-liquid 46 above-mentioned section, the colloidal silica (trade name: Snow tex O (20 mass % water dispersion), product made from Nissan Chemistry) 4 section was added, and the target pigment distribution object for protective layers was obtained.

[0164] - The water distribution object (trade name-ROXEL B.D, product made from I.C.I) 3.5 section of 1-2 bends iso thiazoline 3 ON and the ion-exchange-water 1950 section were mixed in the preparation-amylum-tritici (trade name: amyllum-tritici S, product made from Up-and-coming Food Industry) 220 section of protective layer mat agent dispersion liquid, it distributed to homogeneity, and the mat agent dispersion liquid for protective layers were obtained.

[0165] In the vinyl alcohol-alkyl vinyl ether copolymerization object (trade name: EP-130, DENKI KAGAKU KOGYO K.K. make) water-solution 1000 section of preparation-4 mass % of the spreading blend liquid for protective layers, - Butyl (4-nonyl phenoxy trioxyethylene) sulfonic-acid sodium The 30 sections, the N-(perfluoro-1-octane sulfonyl)-N-propylamino potassium acetate salt (trade name: megger fuck F-120 (2 mass % water solution) Dainippon Ink & Chemicals, Inc.) 30 section, (Sankyo Chemical Co., Ltd. make (2.0 mass % water solution)) Said pigment dispersion-liquid 90 section for protective layers, said mat agent dispersion-liquid 16 section for protective layers, and the zinc stearate dispersion-liquid (trade name: product made from L111 (21 mass % water solution) Chukyo Fats and oils) 45 section were mixed to homogeneity, and the spreading blend liquid for protective layers was obtained.

[0166] On the <spreading of each coating liquid for heat-sensitive recording layers> aforementioned under coat, said coating liquid for heat-sensitive recording layer A, In order of said coating liquid for interlayers, said coating liquid for heat-sensitive recording layer B, said coating liquid for interlayers, said coating liquid for heat-sensitive recording layer C, said coating liquid for light transmittance adjustment layers, and said coating liquid for protective layers, at the spreading rate of 60 m/min It applied by seven-layer continuation, and on 30 degrees C, 30% of humidity, 40 degrees C, and the conditions of 30% of humidity, it dried, respectively and the multicolor thermal recording ingredient was obtained.

[0167] solid content coverage -- a heat-sensitive recording layer A -- 6.0 g/m² and an interlayer -- it adjusted and 3.0 g/m² and a heat-sensitive recording layer B applied so that 5.0 g/m² and a light transmittance adjustment layer might serve as 3.0 g/m² and a protective layer might serve as [6.0 g/m² and an interlayer / 3.0 g/m² and a heat-sensitive recording layer C] 1.5 g/m².

[0168] (Example 2) the barium-sulfate dispersion-liquid 46 section -- receiving -- colloidal silica (trade name: -- the Snow tex O (20 mass % water dispersion) --) It replaces with having added the 4 made from Nissan Chemistry section, and having produced the pigment dispersion liquid for protective layers. It was made to be the same as that of an example 1 except having added the colloidal silica (trade name:

Snow tex O (20 mass % water dispersion), product made from Nissan Chemistry) 8 section, and having produced the pigment dispersion liquid for protective layers to the barium-sulfate dispersion-liquid 42 section.

[0169] (Example 1 of a comparison) It was made to be the same as that of an example 1 except having produced the pigment dispersion liquid for protective layers, without adding colloidal silica (trade name: the Snow tex O (20 mass % water dispersion), product made from Nissan Chemistry).

(Example 2 of a comparison) the barium-sulfate dispersion-liquid 46 section -- receiving -- colloidal silica (trade name: -- the Snow tex O (20 mass % water dispersion) --) It replaces with having added the 4 made from Nissan Chemistry section, and having produced the pigment dispersion liquid for protective layers. It was made to be the same as that of an example 1 except having added the colloidal silica (trade name: Snow tex O (20 mass % water dispersion), product made from Nissan Chemistry) 2 section, and having produced the pigment dispersion liquid for protective layers to the barium-sulfate dispersion-liquid 48 section.

[0170] (Example 3 of a comparison) the barium-sulfate dispersion-liquid 46 section -- receiving -- colloidal silica (trade name: -- the Snow tex O (20 mass % water dispersion) --) It replaces with having added the 4 made from Nissan Chemistry section, and having produced the pigment dispersion liquid for protective layers. It was made to be the same as that of an example 1 except having added the colloidal silica (trade name: Snow tex O (20 mass % water dispersion), product made from Nissan Chemistry) 20 section, and having produced the pigment dispersion liquid for protective layers to the barium-sulfate dispersion-liquid 30 section. (Example 4 of a comparison) It was made to be the same as that of an example 1 except having made colloidal silica (trade name: the Snow tex O (20 mass % water dispersion), product made from Nissan Chemistry) into the pigment dispersion liquid for protective layers, without adding the above-mentioned barium-sulfate dispersion liquid.

[0171] (Example 5 of a comparison) It was made to be the same as that of an example 1 except changing the vinyl alcohol-alkyl vinyl ether copolymerization object (trade name: EP-130, DENKI KAGAKU KOGYO K.K. make) water solution of 4 mass % into the polyvinyl alcohol (trade name-VA217C, Kuraray Co., Ltd. make) water solution of 4 mass %.

(Example 6 of a comparison) the barium-sulfate dispersion-liquid 46 section -- receiving -- colloidal silica (trade name: -- the Snow tex O (20 mass % water dispersion) --) It replaces with having added the 4 made from Nissan Chemistry section, and having produced the pigment dispersion liquid for protective layers. It was made to be the same as that of an example 1 except having added the colloidal silica (trade name: Snow tex YL (40 mass % water dispersion), product made from Nissan Chemistry) 2 section, and the ion-exchange-water 2 section, and having produced the pigment dispersion liquid for protective layers to the barium-sulfate dispersion-liquid 46 section.

(Example 7 of a comparison) It was made to be the same as that of an example 1 except changing the zinc stearate dispersion-liquid (trade name: product made from L111 (21 mass % water solution) Chukyo Fats and oils) 45 section into the zinc stearate dispersion-liquid (trade name: product made from L111 (21 mass % water solution) Chukyo Fats and oils) 90 section, and producing the spreading blend liquid for protective layers.

[0172] Measurement shown below was performed.

(Glossiness) It printed with the digital printer "NC-300" by Fuji Photo Film Co., Ltd., and the specular gloss of the black solid section which carried out the print was measured by the 20-degree incident angle with the digital deflection glossmeter "UGV-5D" by Suga Test Instruments Co., Ltd. Glossiness is so good that a figure is large.

(Contact angle) The contact angle of the water of the black solid part printed with the digital printer "NC-300" by Fuji Photo Film Co., Ltd. was measured with the contact angle meter made from Consonance Interface Science (FACE contact angle meter CA-D mold).

[0173] (Head dirt) With the digital printer "NC-300" by Fuji Photo Film Co., Ltd. Apply print energy (9-105mJ/mm²) at random, and the 10000 continuation print of the black solid image of A5 size is carried out. Form status change-ization of the thermal head resistor element front face in print order was measured for the dirt condition of the thermal head after a print with the sensing-pin type surface type-

like measurement machine (the product made from KAL Ten Call, P-11), and the amount of dirt was computed and standardized from the difference. The dirt of a head also has little one where a value is smaller. The above result is shown in Table 1.

[0174]

Table 1

	実施例1	実施例2	比較例1	比較例2	比較例3	比較例4	比較例5	比較例6	比較例7
保護層バインダー	EP130	EP130	EP130	EP130	EP130	EP130	PVA217C	EP130	EP130
保護層顔料	硫酸バリウム:92 粒径20nmのコロ イダルシリカ:8	硫酸バリウム:84 粒径20nmのコロ イダルシリカ:16	硫酸バリウム:100	硫酸バリウム:86 粒径20nmのコロ イダルシリカ:4	硫酸バリウム:60 粒径20nmのコロ イダルシリカ:40	粒径20nmのコロ イダルシリカ:100	硫酸バリウム:100	硫酸バリウム:92 粒径80nmのコロ イダルシリカ:8	硫酸バリウム:100
保護層潤滑剤	ステアリン酸亜鉛 ×1	ステアリン酸亜鉛 ×1	ステアリン酸亜鉛 ×1	ステアリン酸亜鉛 ×1	ステアリン酸亜鉛 ×1	ステアリン酸亜鉛 ×1	ステアリン酸亜鉛 ×1	ステアリン酸亜鉛 ×1	ステアリン酸亜鉛 ×2
黒ベタ印刷面 充満度(20°)	42	41	40	40	44	45	28	34	29
印刷面接触角	88	87	88	87	74	59	84	86	80
ヘッド汚れ (規格化汚れ量)	1.0	1.2	10.2	2.9	3.8	4.0	12.5	3.0	3.2
ヘッド耐久性 TAプリンター-A5サ イズ10000枚印刷で 面質問題なきこと	10000枚印刷で面質低下なし ← いずれも10000枚以下で濃度ムラによる面質の低下や印刷障害が発生 →								

[0175] In the thermal recording ingredient of the examples 1-4 of a comparison, in any case, head dirt was large, and the fall and print failure of image quality by concentration unevenness occurred in the

print of 10000 or less sheets so that clearly from Table 1. To it, in the thermal recording ingredient of examples 1 and 2, there was little head dirt and, as for deterioration of image quality, a 10000-sheet print did not appear, either. Moreover, the thermal recording ingredient of examples 1 and 2 was excellent also in glossiness.

[0176]

[Effect of the Invention] While being able to form the image which has high glossiness according to the thermal recording ingredient of this invention, head dirt is prevented, it can be stabilized and a high-definition image can be outputted.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] In facsimile, the printer, the label, etc., probably in a field, needs have expanded the thermal recording system, and the more highly efficient thermal recording ingredient is called for in connection with it. It is important with the thermal recording ingredient which heats in the image by this thermal head, and records an image, it not only has the head matching nature suitable for the quality of the material, a configuration, etc. of a protective coat of a thermal head, but that it can be stabilized and can output the image of high quality, without generating head dirt and head wear.

[0003] The protective layer which is mainly in the maximum upper layer determines the thermal head fitness of such a thermal recording ingredient, and various examination is carried out about the protective layer for some time. For example, in order to prevent with [to the head by sticking] a beam etc. and to give print fitness, in order to mitigate the dirt of a head further, it is required [addition of a pigment is indispensable, and] to increase the ratio of a pigment or to enlarge particle size of a pigment etc. However, the increment in the ratio of a pigment and expansion of particle size cause the fall of the glossiness by the fall of the smooth nature of the front face of a protective layer etc. as a result, and deterioration of quality produces them. Moreover, by the increment in oxygen permeability, when a diazo compound is used as a color coupler, increase of light exposure natural complexion coloring is also caused.

[0004] On the other hand, in order to carry out the print of the same side 3 times in succession [unlike the usual thermal recording ingredient / are a high speed and high energy and], the skin temperature of a head rises and it is very easy to generate head dirt with a full color thermal recording ingredient from the lubricant of a thermal recording ingredient front face decreasing in number by this at every print etc. However, on quality, since installation of the above general knowledge (increase the ratio of a pigment or enlarge particle size of a pigment) was difficult in order to realize high surface gloss and low light exposure natural complexion coloring, it was a very big technical problem to prevent head dirt etc. and to manufacture the thermal recording ingredient which can be stabilize and can output a high-definition image.

[Translation done.]